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AN EXPERIMENTAL AND THEORETICAL INVESTIGATION
OF THE EFFECT OF API GRAVITY, INJECTION PRESSURE
AND OIL COMPOSITION ON OIL RECOVERY BY HIGH
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AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE EFFECT OF
API GRAVITY, INJECTION PRESSURE AND OIL COMPOSITION
ON OIL RECOVERY BY HIGH PRESSURE
CARBON DIOXIDE INJECTION

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY
MOHAMMED BAKER ALSINBILI

Norman, Oklahoma

1972

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CARBON DIOXIDE INJECTION

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CARBON DIOXIDE INJECTION

By: Mohammed Baker Alsinbili Major Professor: Dr. D. E. Menzie

Much work has already been done to study the effectiveness of the application of carbon dioxide as a secondary method to the recovery of oil. However, the objective of this study is to find experimentally and theoretically the effect of injection pressure and oil gravity on oil recovery by high pressure carbon dioxide injection. During this investigation, it has been found that the composition of the oil plays a great role in controlling the oil recovery. Four heavy oils of different gravities and different compositions were investigated under the effect of different injection pressures. Twelve experiments were made on these oils. Each oil was investigated under the effect of the three pressures, 1500, 3000, and 4500 psig. It is found that increased oil recovery is a function of pressure increase, gravity decrease, and a more favorable composition.

The characteristics of the oils injected, produced, and remaining after production were studied. Molecular weight, gravity, and composition were investigated by using various techniques. The oil composition was first investigated with a chromatograph and then, simultaneously with a chromatograph and a mass spectrometer. This was done by connecting the

column of the chromatograph to the mass spectrometer. The outlet of the chromatograph column was connected to the inlet of the mass spectrometer so that the peak to peak spectrum could be obtained and scanned directly after appearance in the chromatograph.

A mathematical simulation of the experiments was carried out using the composition of the injected oil obtained from the chromatograph and the mass spectrometer, the applied equilibrium pressure, and the reservoir temperature, by employing a flash calculation principle. The theoretical results predicted by a computer program were in very good agreement with the results obtained from the experimental investigation. The overall average discrepancy between the theoretical and the experimental results was 6.4 percent of the average of the experimental results.

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Mohammed Baker Alsinbili

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CHAPTER I

INTRODUCTION

Even though oil is plentiful, it is not inexhaustible. Better oil recovery techniques might alleviate the difficulties of finding new reserves to replace the produced oil. It is realized that inefficient techniques have left more than 50 percent of the oil in the reservoirs. The trapping of residual oil in the reservoir is attributed to capillary forces, which appear at the inter-phase boundaries of the fluids, and to the mobility ratio of the displacing to the displaced fluid. These capillary forces and the mobility ratios could be minimized by bringing the composition of the displacing and the displaced fluids closer together. Miscibility is defined as the ability of two or more substances to mix and to form a single homogeneous phase; an interface is the important factor which controls this phase and influences the fluid flow significantly. This is so because of the small dimensions of the pores which cause the interfacial forces to be relatively large. It might be of interest to answer the questions: "Why does the oil get trapped?" and then, "Why do we have to produce it by the injection of carbon dioxide, LPG or another secondary recovery method?" To clarify these

questions, Figure 1 represents a simplified imaginary model of two pores through which parallel flow is assumed. This, by no means, represents fully the reservoir pores. The reservoir pores are much more complicated and no one really knows what they look like. The reservoir pores are tortuous, of various radii, sizes, and lengths, have different cross sections, and are interconnected. However, Figure 1 might help one understand a simple phenomenon by assuming only two sizes of pores with parallel flow. Generally a porous rock is water wet; since these two pores compete for a limited supply of water flowing through a constriction, the capillary force draws the water faster through the smaller bottom pore than through the larger upper pore. Therefore, some oil is left in the larger pore by the time the small pore is completely flushed of oil by water. The oil in the upper pore is now trapped. It is noticed that capillary forces will not move the droplet due to the fact that the oil-water interface must flow through a smaller diameter channel at the down-stream end than at the upstream end. Therefore, there is a greater capillary pressure aiding the entry of water on the downstream side of the pore. This is basically why residual oil is left behind in a water displacement. If there were no interface between the two fluids and if both of them were alike in having the same character of fluid to rock wettability, then the oil would not be trapped. The trapped oil, then, can be attributed to the resistance of these small pores saturated with water to

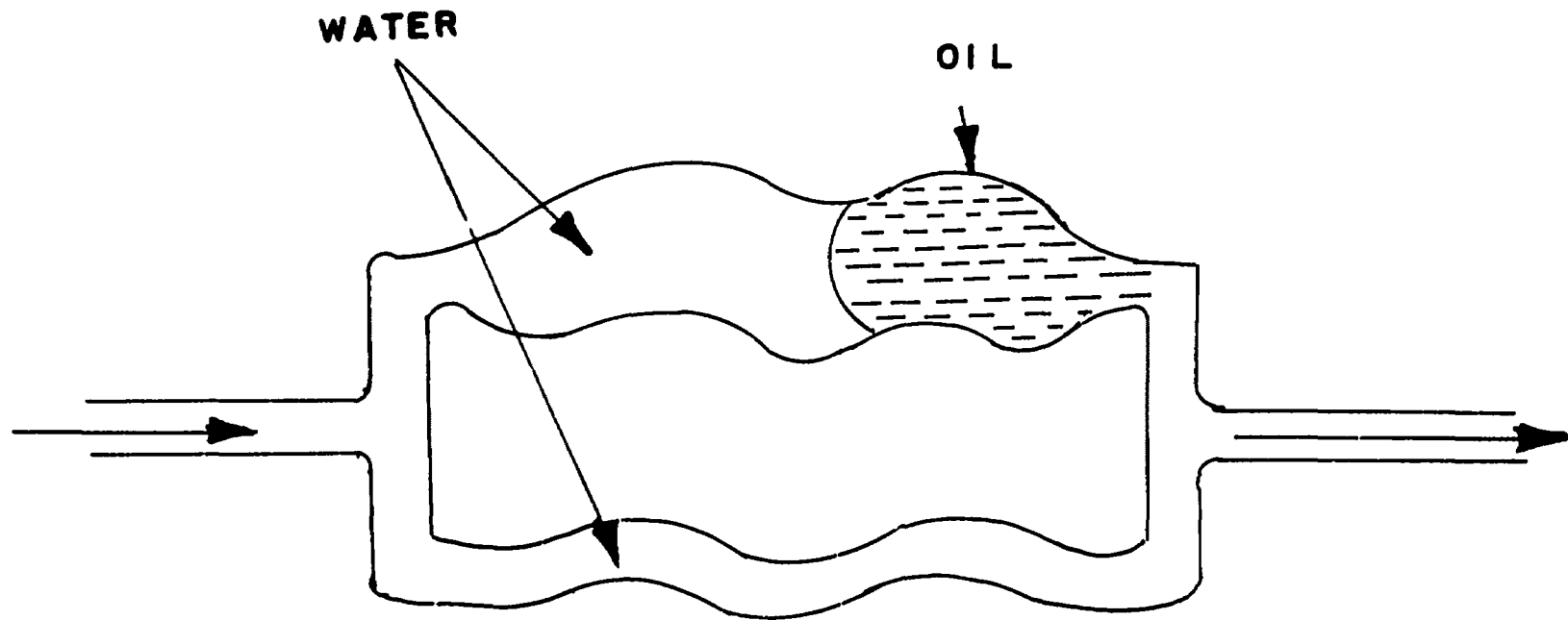


FIG NO. (1)

EFFECT OF CAPILLARY FORCES

the passage of oil. It might also be due to the high mobility ratio of the displacing to the displaced fluid. In other words, the viscosity of the displacing fluid is much less than that of the fluid to be displaced. This will cause fingering which means that much of the oil will be bypassed (not recovered) in unswept pores.

There are many reasons why carbon dioxide injection increases the recovery. Probably the known ones are much fewer than the unknown. These properties will be explained in detail in Chapter V. Carbon dioxide injection increases oil recovery, probably due to the surface tension reduction. This factor is very important in the capillary pressure formula since capillary pressure is directly proportional to surface tension. This surface tension controls the adhesion tension between oil and the rock. Carbon dioxide injection also increases oil recovery by reducing the viscosity of the oil. This property eases the flow of the oil. This fact is evident from Darcy's law which states: the potential drop required to cause the oil to flow, keeping all other factors in the formula constant, is a direct function of the viscosity of the oil. Besides these reductions of surface tension and viscosity of the oil, other factors include swelling of the oil due to good solubility of carbon dioxide in the oil and a good gasification of some of the hydrocarbons into a carbon dioxide-hydrocarbon vapor mixture. These factors are some of the known ones by which carbon dioxide injection gives more

oil recovery. Low vapor pressure of carbon dioxide at reservoir temperature makes the CO_2 easier to use than most natural gases. Natural gases consist of more than 80 percent methane, and methane vapor pressure at a common reservoir temperature is above 7000 psig which is excessive for most reservoirs. There are hindrances to the use of carbon dioxide which must be evaluated before its injection. The high compression cost, corrosion of well equipment, handling difficulties, and unavailability of carbon dioxide are among these drawbacks.

All the beneficial properties of carbon dioxide injection cited were studied in detail and were well established long ago by many workers (2, 8, 12, 14, 26, 35, 36, 39, 41, 44, 45). However, our objective is to determine what will happen to the recovery of oil if the carbon dioxide is injected at varying pressures. How are the effects of gravity and composition on oil recovery changed by the injection of carbon dioxide?

All these effects of pressure, gravity, and composition on oil recovery by high pressure carbon dioxide injection were studied in detail, experimentally and theoretically. Twelve experiments were carried out on four different heavy oils. These oils were different in their compositions and gravities. The result of this study was to determine the importance of these factors in controlling oil recovery by high pressure carbon dioxide injection. The results are presented in the following chapters.

CHAPTER II

LITERATURE REVIEW

Extensive literature is available regarding the use of carbon dioxide in carbonated waterfloods. However, this has not proven to be a useful step in the oil recovery (43). This is because carbonation decreases the viscosity of the water, causing an unfavorable mobility ratio, and thus no additional oil reclamation. Therefore these references are not reviewed in this text. The use of carbon dioxide as an injection fluid to recover oil is not a new idea. A wealth of information is available regarding this topic. A huge amount of work has already been done on the effectiveness, use, advantages, and applications of carbon dioxide in recovering oil. The work of the investigators in this subject area is reviewed here very briefly.

Whorton and Brownscombe (45) were among the first who studied the effectiveness of oil recovery by carbon dioxide injection. In December, 1952, they patented a process for the production of oil from subsurface oil reservoirs through the use of carbon dioxide. Under certain conditions mentioned in their work, carbon dioxide could produce more oil than that recovered by prevailing known methods of oil production.

Holm (12) carried out a laboratory flooding experiment on linear flow systems to study the effectiveness of oil recovery by carbon dioxide injection. He indicated that high oil displacement, approaching that obtained from completely miscible solvents, can be attained by injecting a small slug of carbon dioxide into an oil reservoir and driving it with plain or carbonated water. Holm found that a bank rich in light hydrocarbons was formed at the leading edge of the carbon dioxide slug during the floods on long cores. Formation of this bank was probably due to a solvent extraction by the carbon dioxide, and it is believed this partially accounts for the attractive high oil recoveries. The results of his flooding work on cores of various properties were that 60-80 percent of the original oil in place could be recovered by carbon dioxide-carbonated water flood at pressures of between 900 and 1800 psig. Additional oil (6 to 15 percent of the original oil in place) was recovered by a solution gas drive, resulting from blow-down following the flood. Holm also mentioned that the highest oil recoveries by blow-down were obtained where carbonated water rather than plain water followed the carbon dioxide slug. His conclusion was that solvent flooding with relatively small quantities of carbon dioxide followed by carbonated water at a pressure above 900 psig resulted in oil recoveries from 15 to 50 percent greater than those obtained from conventional water flooding or solution gas drive.

Dunegan (8) studied the possibility of vaporizing crude oil

by gases, such as natural gas, nitrogen, and carbon dioxide, to find out their effect on oil recovery. He concluded that carbon dioxide is the most soluble in oil at the investigated pressures. He found that at a pressure of 4000 psig and a temperature of 135°F, carbon dioxide could recover 56.7 percent of the initial oil in place with a gas cap ratio (reservoir volume of carbon dioxide to the reservoir volume of oil) of 6.4. Beeson and Ortloff (2) also studied the effectiveness of carbon dioxide in recovering oil. Their study was on high and low viscosity crude oil. Ada crude was displaced from linear Torpedo sandstone cores, which is a mildly water wet material having a porosity in the range of 20 to 28 percent and a permeability in the range of 500 to 1500 millidarcy. Ada crude oil is of 400 cp viscosity at 70°F. In the light oil tests, Loudon crude of viscosity 6 cp at 70°F and 38 °API gravity was displaced from linear cores of Weiler sandstone. Beeson and Ortloff concluded that, with Ada crude oil in Torpedo sandstone cores, about 80 percent more oil was recovered by injection of a liquid carbon dioxide bank of 1.48 pore volume; 72 percent more oil was recovered by injecting a liquid carbon dioxide bank of 0.72 pore volume than by reference water flood recovery. Water flooding applied in the experiments recovered 52 percent and 50 percent of the initial oil in place, respectively. Menzie (24, 26) studied the possibility of vaporization of crude oil by carbon dioxide injection. A 35 °API gravity crude oil of molecular weight

230 was charged to a windowed cell, which was kept at a constant temperature of 135°F. At a pressure of 2000 psig, a certain volume of carbon dioxide was injected into the cell and the cell was agitated until equilibrium was reached. The vapor phase was collected in a separator at atmospheric pressure and analyzed for percentages of carbon dioxide and hydrocarbon. The unproduced oil remaining in the cell was sampled to determine its characteristics. This process was repeated at the same pressure for a second carbon dioxide contact. The remaining oil obtained from the first contact was charged with carbon dioxide, and the vapor phase obtained from the second contact was removed. Both the liquid and the vapor phases were sampled. This process was repeated for the third, fourth and fifth carbon dioxide contacts. The results are presented in Figure 2a. Another volume of the same crude oil was studied under a pressure of 2000 psig by applying the same procedure as above. The vapor phase was formed by lowering the pressure, and the vapor was removed. The unproduced oil was charged at 2000 psig with carbon dioxide until the cell pressure reached 3000 psig. At equilibrium the same procedure as explained above was repeated, and the vapor phase volume was recorded. This remaining oil was also charged with carbon dioxide for the third, fourth and fifth carbon dioxide contacts. At 2000 psig it was charged with carbon dioxide until the cell pressure reached 3000 psig and all other previous steps were repeated. The results of these

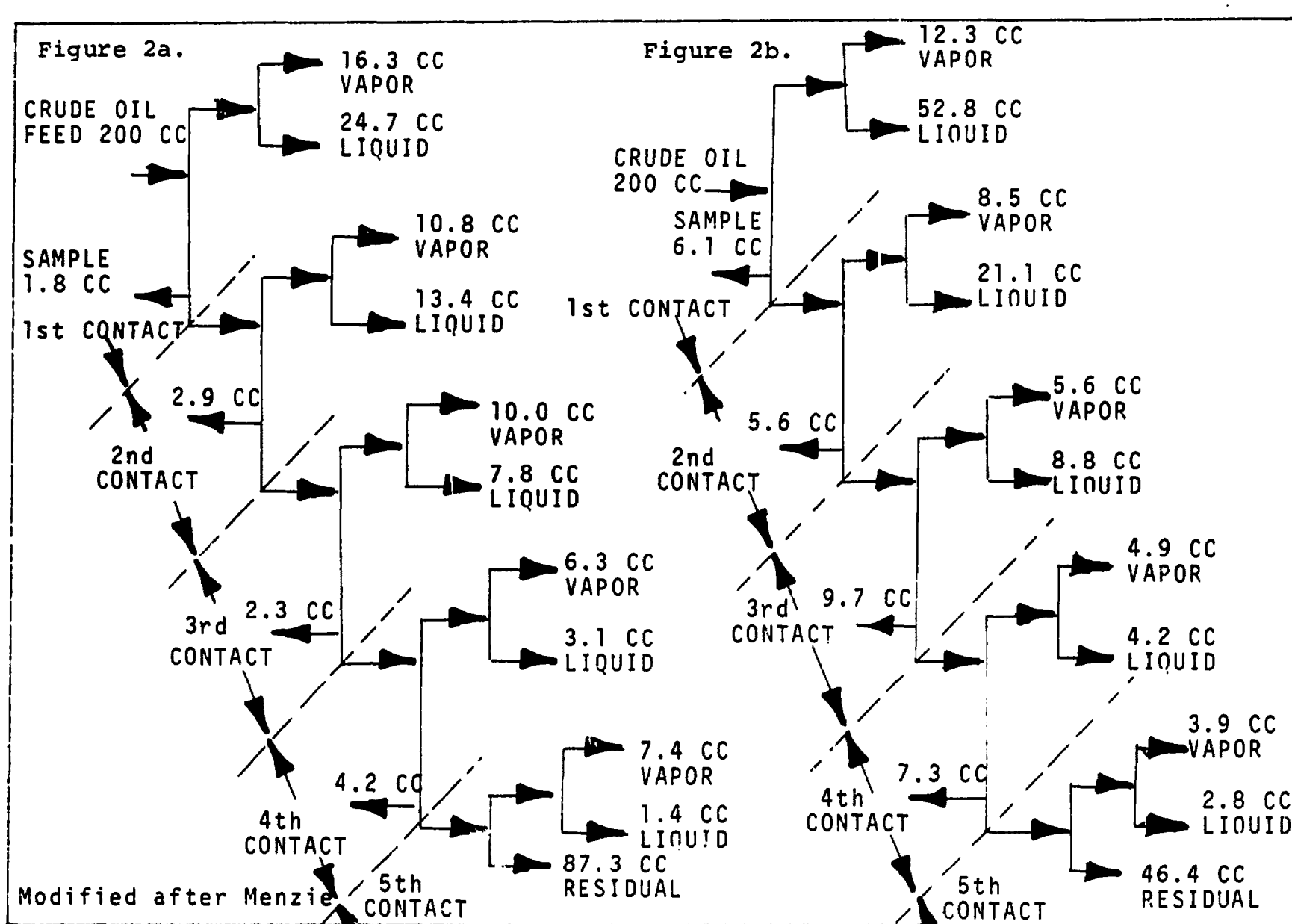


Figure 2. Vapor Liquid Equilibrium Study for Crude Oil CO₂ System at 2000 psig and 135°F (left) and at 3000 psig and 135°F (right).

experiments are presented in Figure 2b. Menzie also attempted to evaluate the rate at which injected carbon dioxide would reach equilibrium in a porous medium by performing comparison studies on an open cell and on a sand-filled cell. He concluded from his study that crude oil can be produced successfully from a petroleum reservoir by a process of vaporization of the crude oil by carbon dioxide.

In a recent study on the effectiveness of the use of carbon dioxide in recovering oil, Roohalah (36) described how carbon dioxide was injected as a gas into some of the cores he used and in others was dissolved in water. He concluded that for recoveries at pressures of 800 to 1000 psig, no matter how carbon dioxide was applied, the residual oil saturations were 18.2, 10.5 and 20.81 percent. His experimental results indicated that 60.2, 59.5 and 54.38 percent of the oil in place after the conventional water flooding was recovered from C-1, D-1 and F-1 cores by application of carbon dioxide at the above pressures. The average oil recovery in all water flooded cores was 30.97 percent of the initial oil in place.

The application and the use of carbon dioxide in recovering oil was also investigated by Smith and others (39, 41). They stated that, after a long study by the Sacroc unit engineering committee, the oil industry was going to inject carbon dioxide in the Kelly-Snyder field of West Texas. They plan to use 202 injection wells in an inverted nine spot pattern. Their study showed that 230,000,000 additional barrels of oil

attributable to the carbon dioxide injection project could be recovered. In their model calculation, a slug of carbon dioxide equalling 20 percent of the hydrocarbon volume is needed for optimum oil recovery. They predicted that a carbon dioxide miscible flood will recover additional oil of 15.4 percent of the oil in place over the recovery that could be obtained from waterflood alone.

Holm and O'Brien (14) conducted a pilot test in a small area of the upper Strawn sand in the Mead field in Jones County, Texas, to study the effectiveness of carbon dioxide as an oil recovery agent in a primary depleted reservoir. The test consisted of injecting a small slug of carbon dioxide (4 percent of the pore volume) followed by a slug of carbonated water (12 percent of the pore volume). Prior to the injection of the carbon dioxide, water was injected to raise the reservoir pressure from 115 psig to 850 psig. The investigators concluded that core data and production histories from the carbon dioxide flooded test area, compared with similar data obtained from areas that had been flooded with water, confirmed the results of laboratory experiments which had shown that a carbon dioxide flood recovers 50 to 100 percent more oil than a conventional waterflood.

Rathmell, et al. (35), conducted displacement tests of reconstituted reservoir fluids in Boise outcrops sandstone cores of 6 to 42.5 feet in length using carbon dioxide at reservoir pressures. They indicated that a miscible displacement

may be achieved by carbon dioxide injection at a pressure well below that necessary when methane is the injected fluid. They concluded that the use of carbon dioxide displacements in the reservoir where miscibility may be developed offers the advantage of much lower displacement pressures than does the use of methane. Immiscible displacements by carbon dioxide may yield very efficient recovery of oil by vaporization and swelling of the heavy ends.

White (44) mentioned that the beneficial properties of carbon dioxide in oil displacement have been known for some time and extensively reported in the literature, but there have been few applications of carbon dioxide as a solvent material. He mentioned that industrial employment of carbon dioxide in fluid injection operations started on the wrong foot when these industries mixed carbon dioxide with the injected water to form carbonated water. This was a step backward for improvement of recovery since the carbonation reduces the viscosity of water and gives an unfavorable mobility ratio. When carbon dioxide was directly injected into an oil reservoir as a displacing agent in the Mead Strawn field by Union of California (13), 82 percent more oil was produced than for a similar sized area using waterflood. The residual oil saturation was 10.1 percent in one core prepared to measure the ROS and 5 percent in the second. The residual oil saturation from a waterflood was 23 percent. In addition to the Sacroc project, Shell plans to inject 20,000,000 cf/d into the North

Cross Unit field in Crockett County, Texas. Amoco has received approval for injecting 18,000,000 cf/d into the Cillock South-field in Galveston County, Texas. Atlantic Richfield has approved the injection of carbon dioxide into the Willard unit, Wasson field, in Yoakum County, Texas.

CHAPTER III

EXPERIMENTAL APPARATUS AND MATERIALS

The effect of injection pressure, API gravity and oil composition on oil recovery by high pressure carbon dioxide injection has been studied experimentally and theoretically. Several types of experiments were performed, and therefore, several different types of apparatus and materials were used; they are discussed in this chapter.

Apparatus and Equipment Used in Equilibrium Vaporization Condensation and Carbon Dioxide Injection

Three-Foot Conical Separatory Funnel

This funnel was specially connected to a 4-1/2 foot stainless steel line which was connected to the top of the cell so that a small static head of oil would always exist when charging the cell with oil. This part is shown in Figures 3 and 4.

Equilibrium PVT Cell

An equilibrium visual cell made of stainless steel with 650 cc total capacity was used. Its maximum operating temperature was 350°F, and its maximum operating pressure was 10,000 psig. The weight of the cell was 70 pounds. It

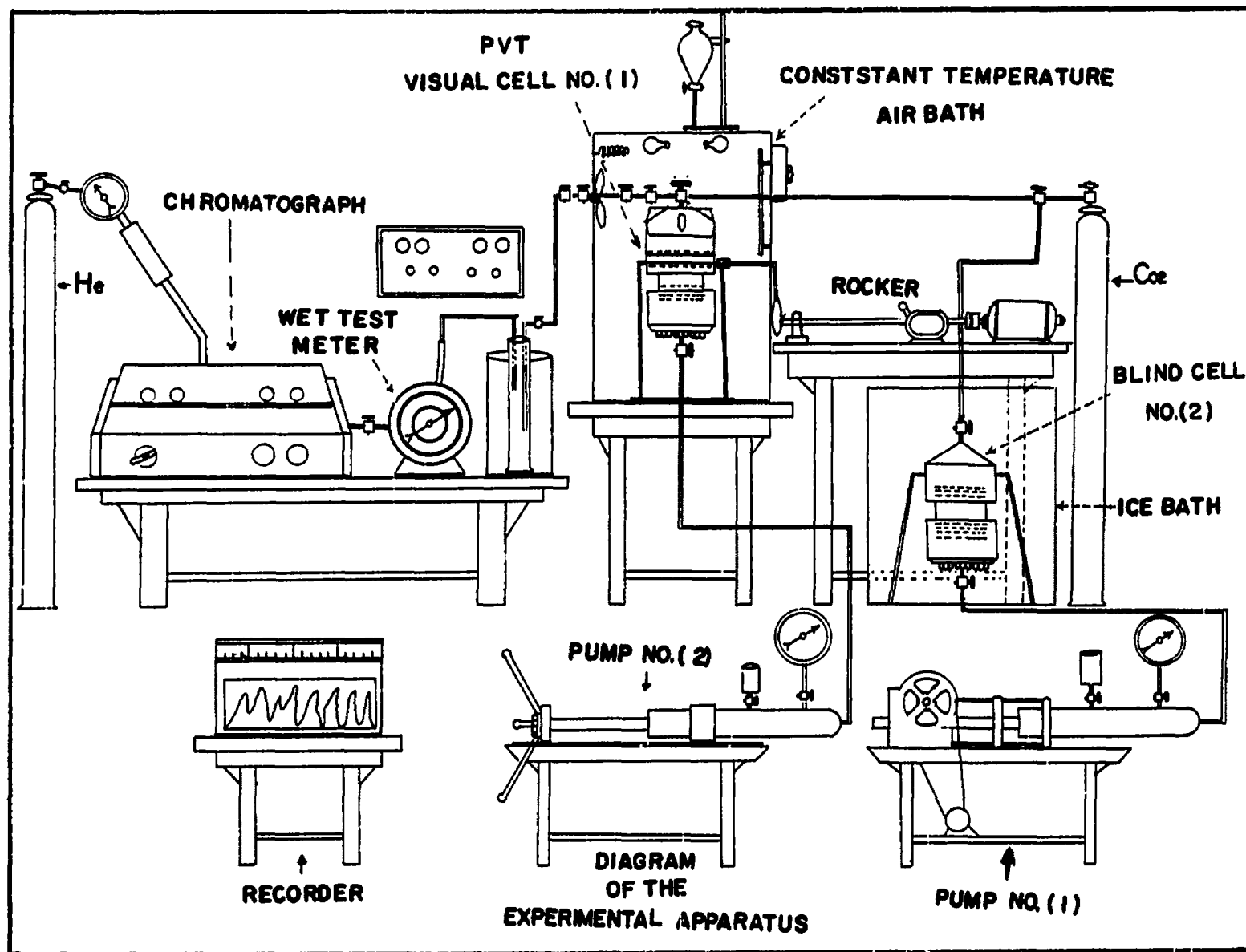


Figure 3. Diagram of the Experimental Apparatus.

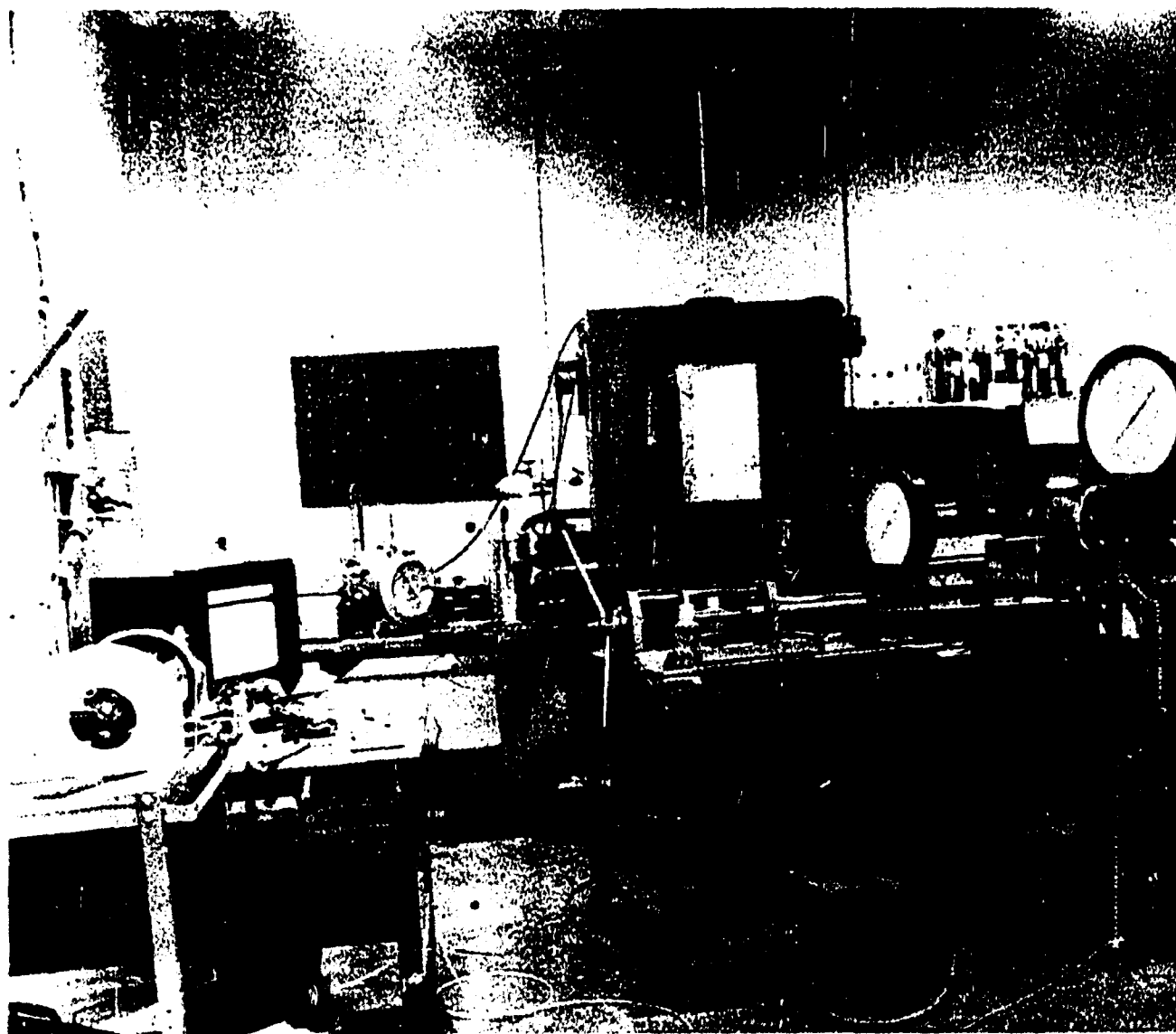


Figure 4. Laboratory Set-Up of the CO₂ Injection Equipment.

was fitted to stand on a circular steel clamp with two extending supports fitted over the cell. The supports were round steel bars which were cradled in a fixed stand. One of the supports was partially drilled to accomodate a connection to the shaft which was connected to a rocking motor. The cell had two stainless steel valves, one in the bottom and the other in the top. The window was made of heat-treated glass approximately one inch thick and was recessed into the main body of the cell. The recess was honed to provide a scratch free seat for the gasket and window. The window was held in place by a heat-treated frame which was ground for flatness and to remove tool marks. It was bolted to the cell body in a manner that eliminated edge strain which might otherwise have cracked the glass.

PVT Blind Cell

This is another equilibrium cell that was used for liquefaction of carbon dioxide. Its volume was 600 cc. Its maximum operating temperature was 350°F and its maximum operating pressure was 25,000 psig. The cell was made from stainless steel, and its weight was 70 pounds.

Heating Bath

This was a constant temperature air bath and was used to house the equilibrium visual cell and the vapor and liquid sampling valves. The air bath consisted of a 3' x 3' x 2' box made of plywood. The inside of the box was insulated with

a 3/4" insulator board and triple layers of aluminum foil which also speeded up the heating process. This box could stand temperatures of more than 250°F. The side of the box facing the operator could be removed by hand. It had a 10" x 20" thick glass window which enabled visual access to the interior of the bath. The bath was heated by two 100-watt bulbs and a heating element. The temperature was controlled automatically by a thermostat. The air inside the bath was circulated by a small fan to keep the entire bath at a uniform temperature. The temperature inside the bath was measured by a thermocouple.

Cooling Bath

This bath housed the blind cell which was used to liquify the carbon dioxide. The bath size was 29" x 21" x 29". The cell was placed on a stand in the cooling bath.

Rocker Assembly

The rocker assembly consisted of a 1/10 horsepower motor with zerox gears to change the rocking speed. The motor was connected to the cell by a coupling and a shaft which was connected to a cam and the zerox gears.

Pumps

One of the pumps was specially designed for this experiment. It was driven by a motor and it could be operated at four different speeds. Its capacity was 100 cc. It was

made of stainless steel, and it was calibrated to 1/100 of a cubic centimeter. This pump was used to liquify carbon dioxide and was also used to charge the equilibrium visual cell. Another pump of 250 cc capacity, calibrated to 1/100 of a cubic centimeter, was used in this experiment; it was made of stainless steel. A third pump was another high pressure volumetric pump of 100 cc capacity which was used as an auxiliary pump if any one of the other two pumps failed; it was made of stainless steel. A 25,000 psig Heise pressure gauge with 50 psig divisions was attached to the pump.

Condensation Equipment

This consisted of several two foot long, 1/8" diameter stainless steel high pressure connection lines with three valves. One was on top of the cell; the other one was used as an exit valve to bleed off excess gas. A third valve was used on top of the atmospheric separator. A small wrapping heater was put around the third valve to prevent the valve from freezing due to the gas expansion. This separator was housed in a large cooling ice bath which was used to condense the vapor and separate the condensate. A wet-testmeter was used to measure the quantity of gas liberated from the system. It was manufactured by Refinery Supply Company and it was calibrated to 1/1000 of a cubic foot.

Chromatograph

A more detailed description of the chromatograph appears later with the description of the mass spectrometer in Appendix A. A GC-2 Beckman gas chromatograph was used to analyze the vapor after it was stripped out of the condensate in the atmospheric separator. This chromatograph is a dual detector having matched pairs of filaments with symmetrical reference and sensing cell geometries. The column of this chromatograph was designed in the laboratory. A 12-foot length and 1/4" diameter column was packed with [BIS 2(2 methoxy ethoxy) ethyl] ether (Trademark BMEE). This packing material was recommended by Reference 31. The carrier gas was helium. The temperature of the column was kept at 40°C. The sample was introduced through the gas sampling valve. This chromatograph was connected to a 1 mv potentiometric Bristol strip chart recorder. More detail about this equipment is in catalogue No. 545E, Beckman instruction manual, GC-2 Gas Chromatograph.

Auxiliary Equipment

An iron-constantan thermocouple was imbedded in the equilibrium cell wall to measure its temperature. A thermometer specially imbedded inside the cell was also used. A highly sensitive Leeds and Northrup potentiometer having an accuracy of 0.001 mv was connected to the thermocouple and measured the temperature to within $\pm 0.05^\circ\text{F}$. There were also two thermometers in the air bath although it was automatically

controlled so as to maintain a 100°F temperature. Figure 4 shows a laboratory setup of this equipment.

Valves, Fittings, Tubing

In this investigation a 1/8" outside diameter stainless steel tubing capable of withstanding a maximum pressure of 15,000 psig was used. All the valves and fittings were also made of stainless steel (by Autoclave Company) and could stand pressures up to a maximum of 15,000 psig.

Specific Gravity and Molecular Weight Apparatus

The specific gravities and molecular weights of all the oil samples, condensates and residuals at all the operating pressures were measured.

The densities of the samples were obtained with a pycnometer and an accurate analytical balance which was capable of reading up to the fourth decimal of one gram. To minimize the errors, the size of the pycnometer was chosen to be as large as possible, 25, 10, 5, 2, 1 cc depending on the amount of the sample. Sometimes a hydrometer was used to check the API gravity if a large amount of the sample was available. To measure the molecular weight, standard Beckman freezing point depression equipment was used. Figure 5 represents the schematic diagram of the equipment which consists of:

1. An inner test tube which contains the solution benzene, a stopper, and a thermometer.

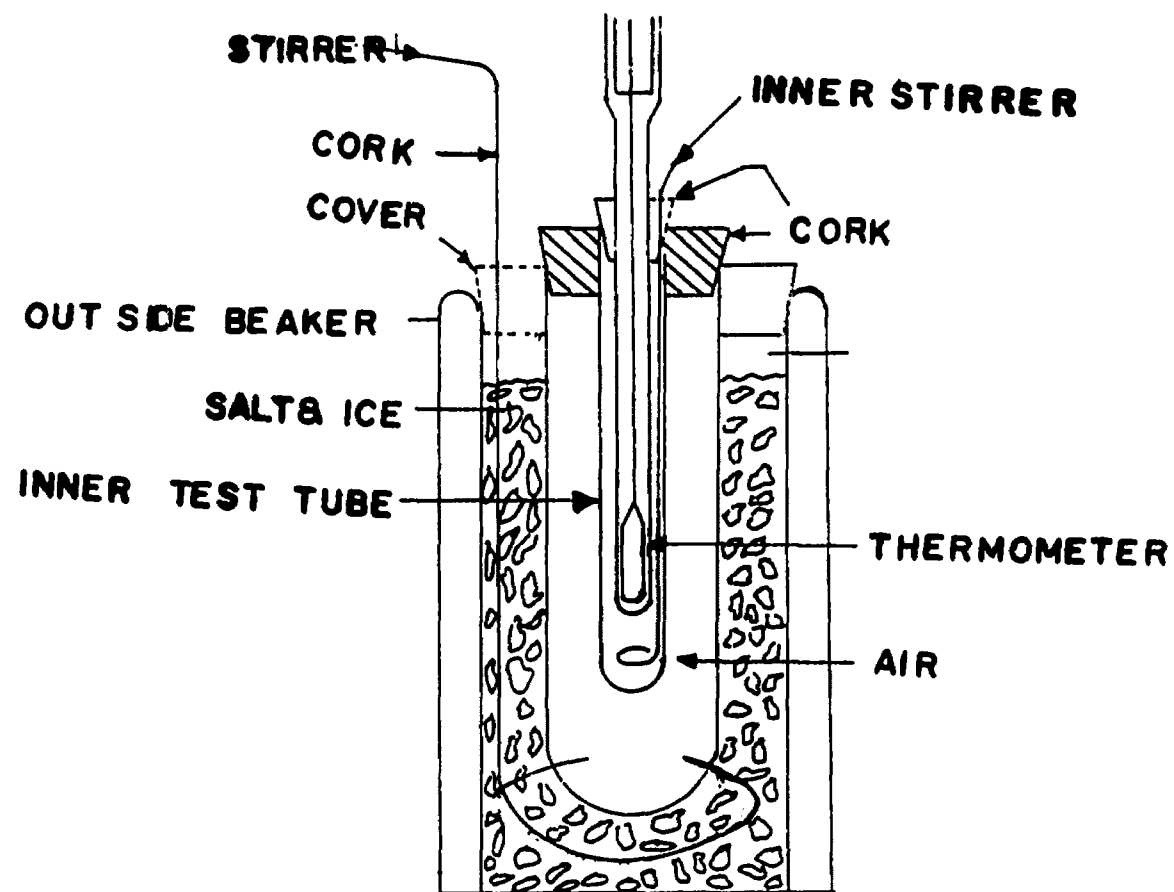


FIGURE 5.

MOLECULAR WEIGHT APPARATUS

2. A Beckman thermometer used in reading the freezing point temperature of the solution.
3. A stirrer inside the inner test tube.
4. Ice, salt, and a cooling bath surrounding the inner test tube which is insulated with an air space.
5. A large beaker which contains the ice-salt cooling solution and the outer stirrer.

Chromatography and Mass Spectrometer

More detail about the theory, the development, the importance and the application of the above equipment is presented in Appendix A.

Chromatograph

The chromatograph was used in this investigation to determine the composition of the injected oils. The mass spectrometer was used with the chromatograph to identify the components of these oils. This work was necessary for the theoretical investigation.

Figure 6 represents a special kind of chromatograph which was used in this investigation called a flame ionization detector. In this chromatograph the effluent gas from the column is mixed with hydrogen and burned in the air. Ions and electrons formed in the flame enter the electrode gap, decreasing the gas resistance, thus permitting a current to flow in the external circuit. When the flame ionization was first introduced in 1958, it was assumed that thermal ionization

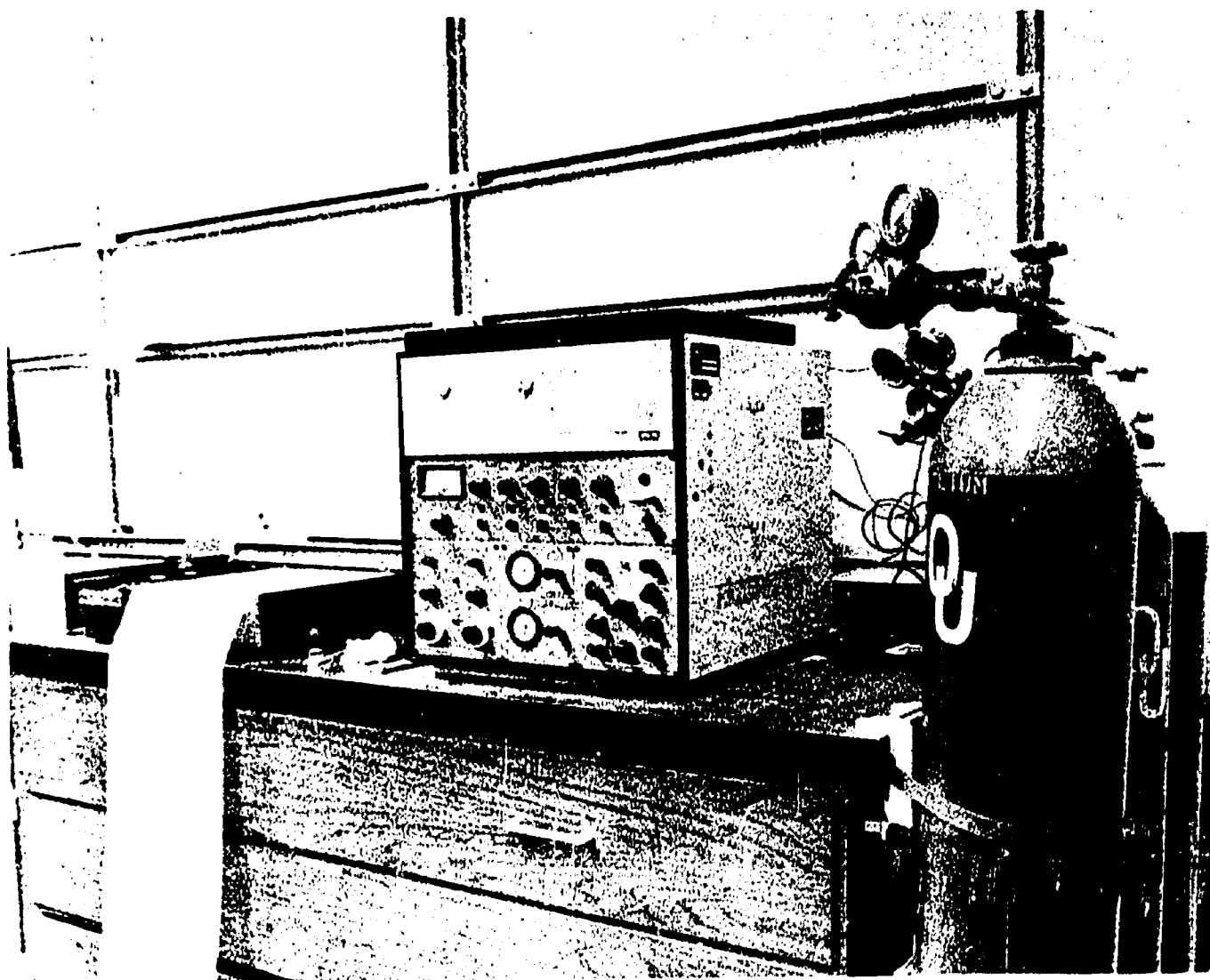


Figure 6. Chromatograph.

was the operating mechanism. Recent studies indicate that thermal ionization may play only a minor role in the overall ionization. A Varian gas chromatograph, Series 1700, with dual ionization detectors was used in this investigation. Another Varian gas chromatograph of the flame ionization detector type, Series 1200, was used simultaneously with the mass spectrometer (see Figure 7). A stainless steel capillary column, chosen according to Reference 17, was constructed in the laboratory; it was 12 feet in length and 1/8" in diameter. The stationary phase was (OV-1) Methyl siloxane. The column support was gas chrom Q.

Mass Spectrometer

The mass spectrometer used in this investigation was an RMU 6E, manufactured by Hitachi Company (11) (see Figure 8). Either a gas, liquid, or solid can be analyzed. If the sample is gas, as is normally the case, it is first introduced into the metering volume where its pressure is measured; then it is expanded into the inlet sample bottle. If the sample is a liquid, a known amount of the liquid is first sealed in a small glass ampule. This ampule is sealed to the metal break off compartment with wax. There the sample is broken off under vacuum and allowed to expand into the inlet sample bottle. If it is solid, then usually it is dissolved in a known solvent and then treated as a liquid sample. The pressure in the inlet sample bottle is sufficiently low so that



Figure 7. Chromatograph and Spectrometer.

the liquid sample is in a vapor phase. The sample is then allowed to flow through the ionization chamber by the opening of the stopcock immediately ahead of the orifice. This is designed to maintain a constant flow of the sample through the ionization chamber. Then the gas is subjected to electron bombardment which converts some of the neutral molecules into positive ions. Electric and magnetic fields then act on these ions to form a fan of ion beams; each beam contains ions of one mass only. By changing the electric or magnetic fields, these fans of ion beams will be forced to sweep out past the exit and to impinge successively on the target. In the target there is an amplifier fed into a galvanometer which deflects through an angle proportional to the abundance of the ions in each beam. The galvanometer deflections are recorded on sensitized photographic paper at a uniform rate. This graph is called the mass spectrum of the sample.

Characteristics of the Mass Spectrometer

The mass spectrometer used in this investigation is a Hitachi Model RMU 6E (11). The analytical measurements were taken with the following readings:

Mass range	=	300 V
Chamber voltage	=	80 V
Total emission	=	800 MA
Target current	=	40 MA
Repeller voltage	=	5 to 10 V

Lense voltage	=	3600 V
Grid voltage	=	-8 V
Chamber temperature	=	250°C
Orifice conductance	=	0.3 cc/sec
Input resistance amplifier	=	1 x 1" ohms
Source exit aperture	=	0.02 mm

Materials Used

Four different oil samples, O_1 , O_2 , O_3 , and O_4 , were obtained from different oil reservoirs. Those samples are described in Appendix B. Carbon dioxide, 99.9 percent pure, was used as the injection gas to recover the oil. Benzene C_6H_6 obtained from the Fisher Company was used to measure the molecular weights of the oil samples. It was free of Thiophene and its water content was 0.02 percent. Its freezing point was 5.7°C. Natural gas used to calibrate the GC-2 gas chromatograph column was obtained from Phillips Petroleum laboratories. The packing of the 20 foot length, 1/4" diameter copper column, was 50 grams of [BIS 2(2 methoxy ethoxy) ethyl] ether. The other column which was used (Varian Series 1700 and 1200 gas chromatograph) was made of a 12 foot length stainless steel tubing of 1/8" diameter; it was packed with the stationary phase (OV-1) of Methyl siloxane and solid support gas Chrom Q of 100/120 mesh size. Much ice and rock salt were used. All the connections were of stainless steel of 1/8" diameter and 15,000 psig maximum working pressure. Swagelok high pressure valves were used.

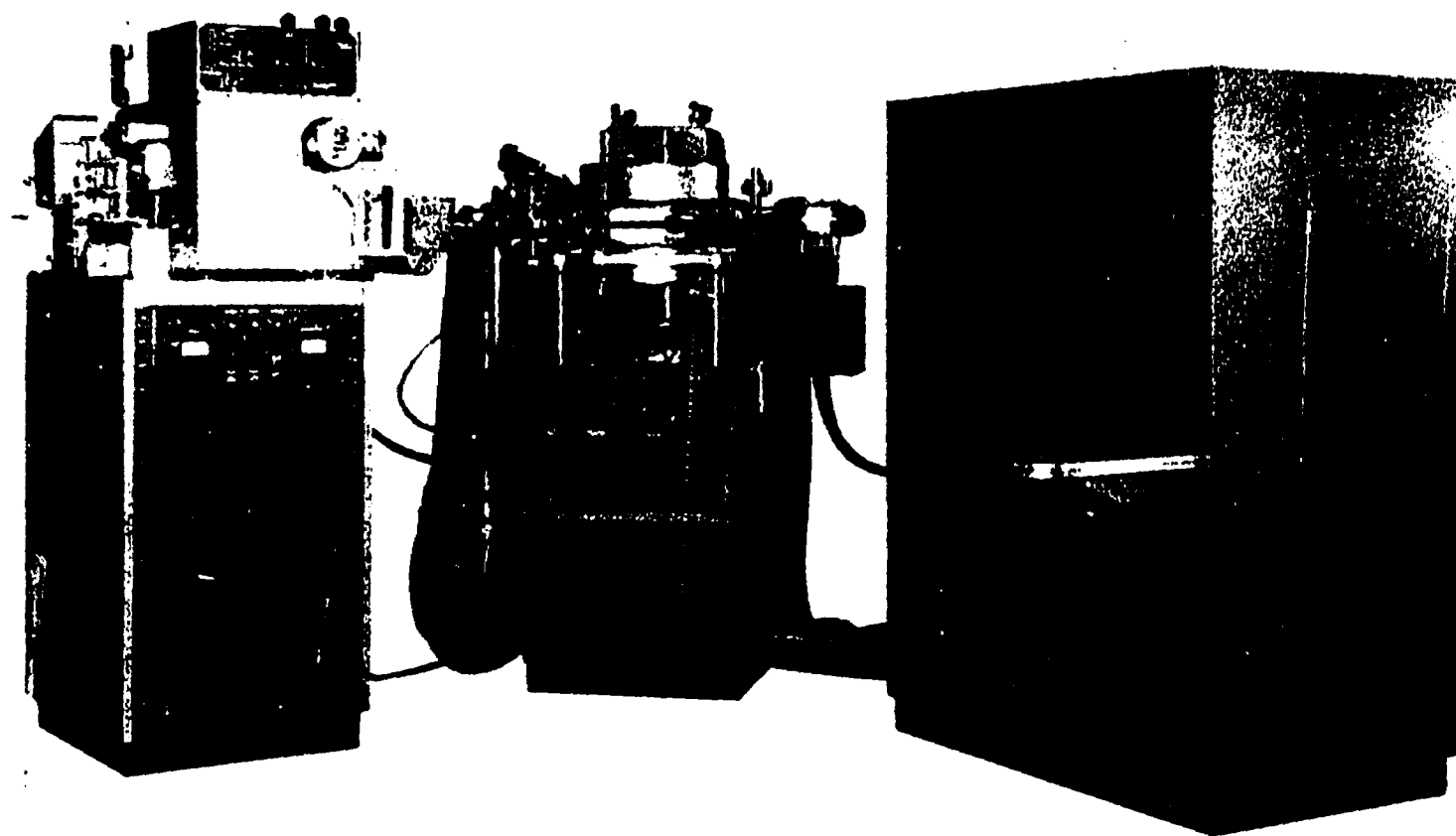


Figure 8. Spectrometer.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Separate experimental procedures were required for determining the composition, specific gravity, molecular weight, and evaporation and condensation.

Evaporization and Condensation

The prime purpose of this investigation was to determine the effects of oil gravity and pressure on oil recovery by high pressure carbon dioxide injection. To achieve these objectives, four oils of 30.2, 24.3, 22.7, and 15.4 °API gravity were investigated. Each of these oils was subjected to the effects of three pressures, 1500, 3000 and 4500 psig. Before beginning, the amount of gas required for each experiment, such that the gas caps would all have the same volume, was calculated in order to eliminate another experimental variable. The investigation was then carried out under constant temperature, constant pressure, constant oil volume and a gas cap volume which is as constant as possible. The variables are the equilibrium pressure, oil API gravity and the oil composition. Except for the size of the gas cap, most of these variables could be controlled and could be held constant.

It is difficult to hold the gas cap size constant. In other words, a certain amount of carbon dioxide should be injected into each of the four oils such that the volume of the gas caps obtained at each of the three equilibrium pressures and at constant temperature and constant oil volume will be the same. This was a difficult step. An attempt was made to produce as nearly as possible the same gas cap, but this was not achieved exactly. The amount of carbon dioxide producing the gas cap should be sufficient to vaporize enough oil so that an appreciable amount of condensate for later study is obtained. At the equilibrium vaporization pressure a certain amount of mercury should be in equilibrium in the cell with the carbon dioxide volume injected. This is essential to control and to maintain the equilibrium pressure. Determining the gas cap led to a theoretical calculation. Much thermodynamic and experimental data were used (as will be explained in Chapter V). However, these data were not very helpful and were not suitable to our kinds of oils.

Calibration of the gauges with a dead weight tester was performed prior to each experiment. Calibration of the gas chromatograph GC-2 by a natural gas was also performed. Prior to any experimental step, all the lines and the cell were cleaned with naphtha, then alcohol and dried by a jet of dry air.

Measuring the Equilibrium Visual Cell No. 1 Volume

The top of this cell was connected to a conical visual flask (separatory funnel). A certain mark was labeled on that flask to maintain a certain mercury volume in the cell. It also helped to keep a certain static head of oil above the cell. This also eased the charging of the cell with the oil and prevented air bubbles from entering the cell. The cell was charged with mercury by pump No. 1 (Figure 3). The cell volume was equivalent to that amount of mercury marked on the separatory funnel. The volume in the line connector between the top of the cell and that mark was measured each time the experiment was performed.

Charging the Equilibrium Cell with the Oil Sample to be Investigated

A 275 cc oil sample was measured by a graduated cylinder at 76°F and at atmospheric pressure and it was poured into the conical flask. Then mercury was withdrawn from the cell very slowly. Depending on the oil viscosity, the duration of each oil input was between 8 and 72 hours. This slow charging of oil was to prevent oil evaporation and the entrance of vapor bubbles into the cell. After charging with oil, the top valve of the visual cell was closed. The volume of mercury withdrawn was recorded from volumetric pump No. 1 and the volume of oil charged to the cell was recorded.

Charging the Cell with Carbon Dioxide

A blind equilibrium cell (No. 2) (Figure 3) was installed in a special cooling ice bath. The temperature of the cell was held between 33° and 35°F. Then the top of this cell was connected to a large carbon dioxide cylinder. Mercury was withdrawn from the cell until a certain volume of carbon dioxide entered the cell at the carbon dioxide cylinder pressure. This volume of carbon dioxide was precalculated to give enough liquid carbon dioxide injected into cell No. 1 to produce approximately the same size gas cap. The volumes of carbon dioxide withdrawn from the cylinder at the cylinder pressure are presented in Table 1. The carbon dioxide volumes were read from pump No. 1. The top valve of the carbon dioxide cylinder was closed. The volume of carbon dioxide to be injected was fed into cell No. 2, after being compressed to a pressure of 1500 psig. This volume of liquid carbon dioxide was recorded and is presented in Table 1. The oil and mercury in cell No. 1 were compressed to 1500 psig. The volume of mercury required for compression was recorded and is presented in Table 2. The volume of mercury withdrawn from cell No. 1 was recorded from pump No. 2 and is presented in Table 1. The carbon dioxide injected into the equilibrium cell was in a liquid form since the critical temperature of carbon dioxide is 87.8°F and its critical pressure is 1073 psig, while the compression pressure in the experiment was 1500 psig and the temperature was held down to 33°F.

TABLE 1

EXPERIMENTAL VOLUME OF CARBON DIOXIDE AT THE INDICATED PRESSURE

Pressure psig	Oil Gravity °API	Volume of CO ₂ at its Cylinder Pressure cc	Volume CO ₂ com- pressed in the Blind Cell at 1500 psig and 33°F cc	Volume CO ₂ charged into Visual Cell at 1500 psig and 33°F cc
1500	30.2	278.000	263.000	203.039
3000	30.2	415.900	367.000	280.639
4500	30.2	263.318	243.618	224.106
1500	24.3	228.000	215.876	203.290
3000	24.3	376.800	353.159	250.602
4500	24.3	276.390	262.000	221.166
1500	22.7	259.519	237.505	191.693
3000	22.7	250.438	229.438	206.339
4500	22.7	284.608	260.831	200.923
1500	15.4	271.511	250.690	208.225
3000	15.4	256.520	236.520	197.165
4500	15.4	259.143	239.140	217.584

TABLE 2
VOLUME OF MERCURY REQUIRED TO COMPRESS CELL CONTENTS
AT THE INDICATED PRESSURE

Oil Sample	Oil Gravity °API	Mercury required from 0 to 1500 psig cc	Mercury required from 0 to 3000 psig cc	Mercury required from 0 to 4500 psig cc
O ₁	30.2	5.242	30.480	39.775
O ₂	24.3	5.883	28.448	37.763
O ₃	22.7	3.278	23.708	38.240
O ₄	15.4	3.700	30.163	52.828

Injection into the Equilibrium Visual Cell

The carbon dioxide was used here as a means to vaporize and recover the oil. This was done in three parts depending on the equilibrium pressure under which the experiment was performed.

1500 psig equilibrium pressure: Prior to charging the visual cell with carbon dioxide, the top valve of the cell was closed. Then the oil and mercury in the cell compressed to the equilibrium pressure of 1500 psig by pump No. 2 (Figure 3) and a reading was taken. This reading was recorded since it indicates the oil volume at the equilibrium pressure and is presented in Table 2. The carbon dioxide cylinder valve was closed to compress the contents in cell No. 2 to the same equilibrium pressure. A special stainless steel connection between the tops of cell No. 2 and cell No. 1 was installed. Then mercury was injected from pump No. 1 into cell No. 2 to displace the liquid carbon dioxide at the equilibrium pressure, while pump No. 2 was withdrawing mercury from the visual cell No. 1 until the required volume of carbon dioxide was injected. Then the top and bottom valves of cell No. 1 were closed. All the extra connections were removed. Four different experiments were performed at this pressure, one for each different gravity oil.

3000 psig equilibrium pressure: Four experiments were performed at this pressure. The procedure is similar to that of the 1500 psig procedure with the carbon dioxide in cell No. 2

compressed to 1500 and the oil and the mercury in cell No. 1 compressed to 1500 psig. The 1500 psig readings were recorded. Then carbon dioxide was charged into the visual cell at 1500 psig by injecting mercury from pump No. 1 to the bottom of cell No. 2. CO₂ was injected into the top valve of the visual cell No. 1 which was then closed and all carbon dioxide connections were removed. The oil, the carbon dioxide, and the mercury were compressed from the 1500 psig pressure to the required equilibrium pressure of 3000 psig. The volume of mercury which was required for the compression is recorded in Table 2, Column 3. This reading is actually the cumulative readings of the mercury volume required to compress the oil and mercury from zero to 1500 psig and the volume which was required for the compression of the cell fluids from 1500 to 3000 psig. Then the bottom connections from the visual cell to pump No. 2 were removed.

4500 psig equilibrium pressure: Another four experiments were performed at this pressure. The steps followed here were similar to these in the previous two procedures except that the cell fluids were compressed to a 4500 psig equilibrium pressure. Table 2, Column 3 values are the sum of the mercury volumes that were required to compress the oil and mercury from zero to 1500 psig and the mercury volume which was required to compress the oil, mercury and the gas cap in the cell from 1500 to 4500 psig.

A thermometer was set in position to assist in reading the temperature inside of the cell. The iron and constantan thermocouple was also hooked into position on the cell and then was connected to a potentiometer. There was also a special automatic thermostat to control the bath temperature to 100°F and a fan to circulate the air throughout the entire bath.

The heating bath cover was put back to close the bath. There was a glass window in the air bath to assist in observing the inside of the bath and to facilitate the reading of the cell temperatures.

Rocking the Cell

The cell was rocked by a special mechanical device consisting of a cam, shaft, speed reducer with zerex gears, and a 1/10 horsepower motor. The cell was rocked between 36 and 78 hours to achieve equilibrium.

Cell Stand-Still Period

The cell remained at rest for a short period of time so that equilibrium could be achieved. In other words, so that any oil component would not change its concentration in the vapor or liquid phases with time. This period of time was regulated to be between 6 and 28 hours.

Condensation

The condensation procedure was performed by installing a 200 cc graduated cylinder in a large cooling bath which was filled with ice for about 3 to 4 hours prior to the condensation.

This arrangement was to substitute as an atmospheric separator. The graduated cylinder had two openings which came out of the top of the cork which was sealed with wax. One opening was a continuation of a 3 foot length, high pressure stainless steel 1/8" diameter line, connected to the top of the visual cell and was controlled by four high pressure Swagelok valves. One of those valves was on the top of the visual cell. The second valve was used as an exit for a bleed-off emergency. The third valve was near the separator and was wrapped with a special heating element to prevent freezing of the valve. The fourth valve was between the top and exit valves. These valves were all for safety and to give more control of flow from the cell. The other opening from the graduated cylinder was to carry the stripped gas to a wet-testmeter for volume measurement. There was a connection with a valve to the chromatograph to analyze the gas coming out of the graduated cylinder. The condensation was done as slowly as possible. This was to avoid an explosion in the separator and to prevent any carryover to the wet-testmeter; it took 5 to 6 hours. The condensation was started by the cracking of the top valve of the equilibrium visual cell. The bottom valve of the cell was connected to pump No. 2 (Figure 3) and was opened after building equilibrium pressure in the pump. The other three valves except the exit valve on the top line connection were also opened slowly. The equilibrium pressure was maintained continuously in the visual cell since the vapor phase was

displaced by injecting mercury. It was watched through the window glass of the cell until the last bubble of the vapor phase had been removed from the cell. Then the top and bottom valves of the cell were closed. The pressure of the carrier gas supplied to the GC-2 gas chromatograph was 29 psig. The column temperature was 40°C, the Katherometer current was 350 ma, and the attenuation was 100.

Preparation of the GC-2 Gas Chromatograph

During the resting period for the cell, the gas chromatograph was prepared. The chromatograph had already been calibrated with a standard gas. The column was made in the laboratory from a 20 foot, 1/4" diameter copper tube line. It was first cleaned with acetone and dried with a jet of dry air. It was packed with 50 gms of "chromb Bis" as recommended by Reference 31. This column did not give good results in the effluent gas obtained from the wet-testmeter. It gave only one large peak which was thought to be carbon dioxide.

Residual Oil

After the last bubble of the vapor phase had left the visual cell, the top valve of this cell was closed. The oil left in the cell was called the residual. This oil was displaced by injecting mercury with pump No. 2 (Figure 3). The displaced oil was collected in a 500 cc graduated cylinder. The bleed-off was through the exit valve. The residual oil

volume was measured after all the gas bubbles had escaped to the atmosphere.

Cell Cleaning

Before each experimental run the cell was cleaned thoroughly. This was accomplished by withdrawing the mercury which remained in the cell after bleeding off all the residual oil. The mercury was withdrawn by gravity effect from the bottom of the visual cell using a long connection. The top of the cell was filled with naphtha by the siphoning action during the mercury withdrawal. When the cell was filled with naphtha, it was shaken for 2 hours, then flushed first with acetone and then with methyl alcohol. The cell was dried by a strong jet of dry air. This was also done to all the connecting lines.

Density and Molecular Weight Measurements

Density

The densities of all the original oil samples, condensates and their residuals were measured on a very sensitive analytical balance. The balance was accurate to the fourth decimal place. Five different size pycnometers were cleaned first with naphtha, then with acetone and then with ethyl alcohol. They were dried by a jet of dry air. The pycnometer used for each measurement was chosen so that the sample volume occupied as much volume as possible. The chosen pycnometer was weighed accurately to the fourth decimal place.

Then it was filled with the sample, and weighed again. The density was measured at 76°F and atmospheric pressure. These measurements are presented in Chapter VI, Table 23.

Molecular Weight

The average molecular weights of the original oil samples, condensates and their residuals were measured by Beckman's standard freezing point depression method. The apparatus is shown in Figure 5. The procedure followed was based on the principle that the ideal solution is the one in which the forces between molecules are not altered when molecules of more than one kind are mixed. Rault's law applied to this kind of solution says that the freezing point depression is directly proportional to the molal concentration of the solution.

The apparatus was cleaned thoroughly, especially the inner test tube. Crushed ice was mixed with rock salt in a 4 to 1 proportion respectively and placed in the larger outside beaker. A certain amount of benzene was weighed and its average freezing point was obtained with the Beckman thermometer. Readings were taken many times and averaged. Then the inner equipment was cleaned and left to dry.

Another amount of benzene was weighed accurately with a small beaker. Several drops of the hydrocarbon sample were added to the benzene and it was weighed to the nearest 0.0001 gm. The solution was then mixed by shaking it. Then it was

poured into the inner test tube. The amount of the added hydrocarbon was controlled to give a reading within the range of the thermometer. Then the solution was stirred with the inner stirrer using an up and down motion. This helped to distribute the heat loss homogeneously. When the first crystal appeared in the solution being in equilibrium with the solution, the freezing point temperature was indicated. However, many readings were taken to avoid the uncertainty. Those measurements are presented in Chapter VI, Table 24. The method of calculation is given in Appendix G.

Composition Determination

Mass Spectrometer and Chromatograph

Chromatograph: The chromatograph which was used to analyze the oil samples, condensates and their residuals was a Varian Series 1700 gas chromatograph. A capillary column of 1/8" diameter and 12 foot length made of stainless steel was used. One of the two chromatograph flame detectors was used. The column used was an OV-1 type. It was constructed in the laboratory as was recommended by Reference 17. A special procedure was followed to operate this chromatograph.

Procedure followed: (See Figure 6) The bottles of hydrogen and air were set to 24 psig and 14 psig, respectively. That was the normal amount of the gas to supply the required flame. The carrier gas was helium. Its cylinder pressure was adjusted to 65 psig which gave a flow rate of approximately

30 ml/min. The pressure indicated by the instrument gauge was 18 psig. Then the main power switch was turned on. This was indicated by a red light. The pen recorder switch was turned on. The B attenuator switch was positioned to infinity to short the recorder terminals. The recorder pen was adjusted to electrical and mechanical zero. The B cell voltage switch was set on the balance position since one detector was used. The mode selector was set on B position. The B range selector was set to the balanced position. The B attenuator switch was set on position 1. The attenuator is dual concentric. The inner control knob is for channel A and the outer knob for channel B. The A control knob was pulled out since the B channel was the only one operating. The B balance control was adjusted to the zero pen recorder. The air, hydrogen and carrier gas helium were checked to be on proper flow rates. The B cell voltage switch was set on the flame position. The B range selector was set to a 10^{-11} amp/mv position. The bucking voltage control was turned to its maximum counter clockwise position to balance the voltage inside the filament. Then the hydrogen flame detector was ignited. This was performed by holding the B cell voltage switch to the IGN position for about three to five seconds. The recorder pen was shifted a large amount off scale indicating that ignition was accomplished. The B bucking control switch was adjusted to rezero the recorder pen. The B range was set on 10^{-11} resistance and the B attenuator was set on a reading to give clearer

peaks such as 4 or 64 depending on the concentration of each component in the oil sample. About 0.4 μL of the sample was injected by a special sampling syringe through the injection block opening. The chart of the recorder was moving at a speed of 0.5 inch/min. The column temperature was kept at 70°C. The detector temperature was 280°C. The injector temperature was 280°C. The procedure which was followed here was to wait for 40 or 50 minutes after injecting the oil sample until all the sample components were analyzed at the 70°C column temperature. Then the column temperature was increased to 250°C for 20 or 30 minutes. This was done to assist in analysis of all the heavy components and to clean them out of the column.

Mass Spectrometer

The mass spectrometer was used to identify the sample components which were obtained by the chromatograph, whether the sample was original oils, condensates or their residuals. This was required for the theoretical investigation. But, because the mass spectrometer was not always available during the investigation, not all the samples were analyzed. However, not all of them were required by the theoretical investigation. What was required was the analysis of the original oil samples only. In other words the feed composition only was required. The procedure which was followed was the same as that used for the chromatograph Varian Series 1700, except

that a chromatograph Varian Series 1200 was connected to the mass spectrometer using the same column. The exit of the column was connected to the inlet of the mass spectrometer so that each peak that appeared on the chromatograph was scanned by the mass spectrometer and was recorded on a special film paper. Much time was required to get all the peaks because the chart length was between 30 and 50 feet. Rather than show these large charts, a composite chart is presented in Figure 39.

Since the mass spectrometer instrument was very complicated, highly sensitive and very expensive, it was run by a special operator. Generally, a 0.2-0.4 μL of the sample was transferred by a very fine capillary glass tube to a liquid sample compartment of the mass spectrometer. A high vacuum was applied to evaporate the sample molecules. Then the vapor of the sample was ionized by applying a high voltage, bombarding the molecules with a high speed jet of electrons. Then those ions were deflected in a certain direction by high magnetic field according to Lorentz's Rule. They were then scanned according to their mass/charge which was plotted by galvanometer on the electric photo paper.

The mass spectrum charts obtained by scanning the sample vapor obtained from the chromatograph are not presented here due to their great length. The results of these charts are presented in Tables 30 through 41. A composite chart of the mass spectrum of sample C_1A is shown in Figure 39.

CHAPTER V

RESULTS OF THE THEORETICAL INVESTIGATION

Mechanism of High Pressure Carbon Dioxide Injection

The mechanism of high pressure carbon dioxide injection is believed to be a high pressure gas injection process. The miscibility in this process is achieved by applying a high pressure which is still less than that pressure required for a lean gas injection such as methane or nitrogen. There may be several reasons why carbon dioxide as well as good oil composition and low oil gravity are controlling factors in the miscibility. Those reasons are reduction of the oil surface tension, which reduces the capillary forces between the wetting and non-wetting phases, reduction of the viscosity of the oil which helps the oil to flow more easily, and the solubility of carbon dioxide in the oil which gives good swelling properties. The size of the two phase region in the ternary diagram is much smaller than that for methane. This might be due to the low vapor pressure of the carbon dioxide. These factors will help in achieving the miscibility with a lower pressure than those obtained with the injection of lean gases. The K values of carbon dioxide are smaller than those of methane or nitrogen at the same pressure and temperature

which means a greater solubility of carbon dioxide in the oil.

There are two mechanisms for miscible processes.

They are:

1. Processes in which the injected fluid and the inplace fluid form a single phase solution for all compositions.
2. Processes in which the injected fluid and the inplace fluid do not form a one phase solution by a single equilibrium contact.

But multiple contacts might generate a zone of continuous single phase composition by causing a mass transfer of components between the injected and inplace fluids. The processes in Class 1 are characterized by first contact miscibility, while processes in Class 2 are like those for enriched gas drive and high pressure gas drive. While the miscible zone in the enriched gas drive is obtained by having the light intermediate hydrocarbons in the injected gas which will dissolve in the oil and enriches it to a state where it becomes miscible with the injected gas, the miscibility in the high pressure gas drive is generated by a transfer of the intermediates from the reservoir fluid into the injected lean gas. Miscibility is achieved by applying the miscible pressure which is defined as that pressure at which miscibility is possible after an initial period of immiscible displacement when sufficient mass transfer of intermediates has occurred to satisfy the requirement for miscibility.

The high pressure gas injection miscibility mechanism in our experiments could be visualized conceptually with a ternary phase diagram constructed from methane, ethane through hexane, and heptane plus. This representation, although not thermodynamically accurate, hence not quantitative, is still useful to illustrate concepts. Briefly, referring to Figure 9, suppose the first increment of gas injected immiscibly displaces some of the reservoir fluid near the injection face and comes to equilibrium with that reservoir fluid which is not displaced. Some overall composition such as C_1 results, which consists of equilibrium gas G_1 and equilibrium liquid L_1 . The gas G_1 is displaced into the reservoir by the second increment of the injected lean gas and contacts fresh reservoir fluid immiscibly, yielding the overall composition C_2 . This overall composition consists of gas composition G_2 and liquid composition L_2 . The gas composition G_2 flows ahead and contacts more reservoir fluid. This process is repeated many times in the reservoir. A simulator for this process was used in the laboratory using high pressure carbon dioxide injection. The reservoir is the cell containing the reservoir oil. The ternary diagram shown in Figure 10 is composed of CO_2 , CH_4 to C_4H_{10} , and C_5H_{12} plus. The two phase region in these ternary diagrams is expected to be smaller than the one presented by Figure 9 due to the favorable characteristics of carbon dioxide in the oil, cited before, which cause a lower miscible pressure requirement (see Figure 10). The simulation

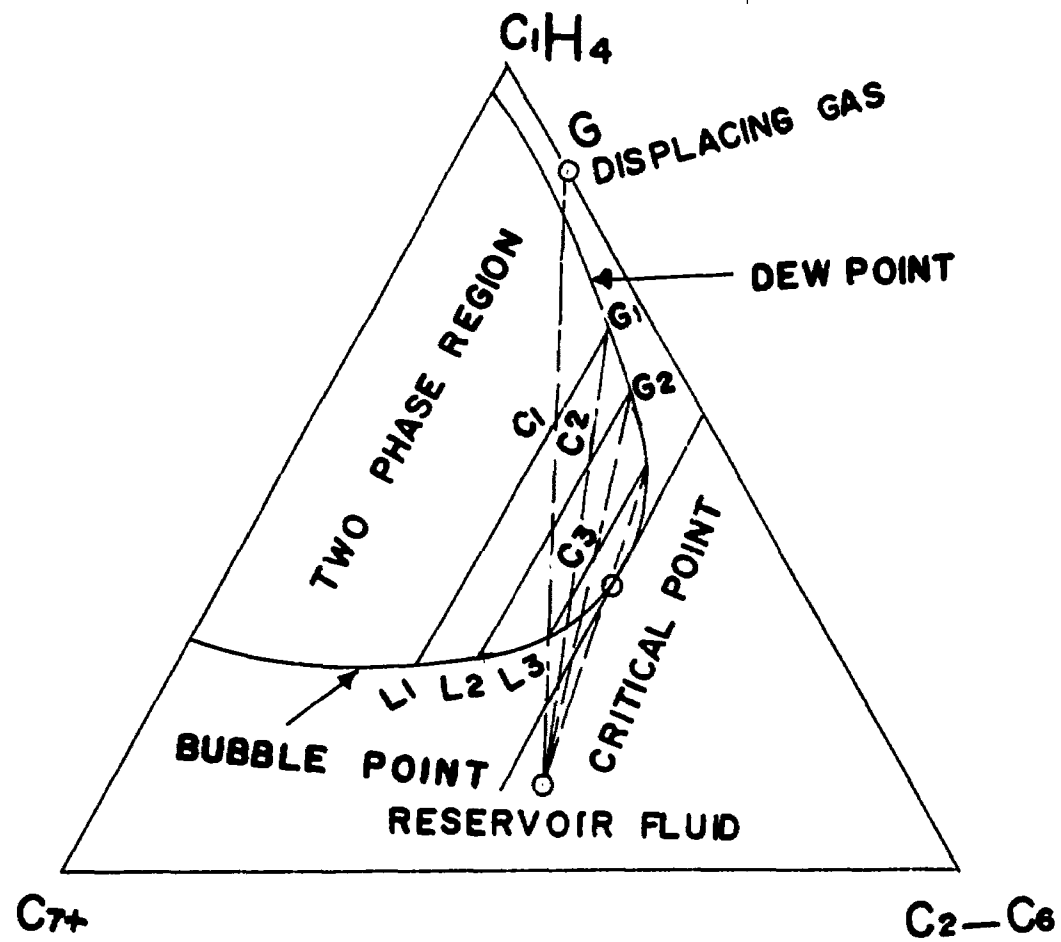


FIGURE 9.

MECHANISM OF HIGH PRESSURE GAS INJECTION

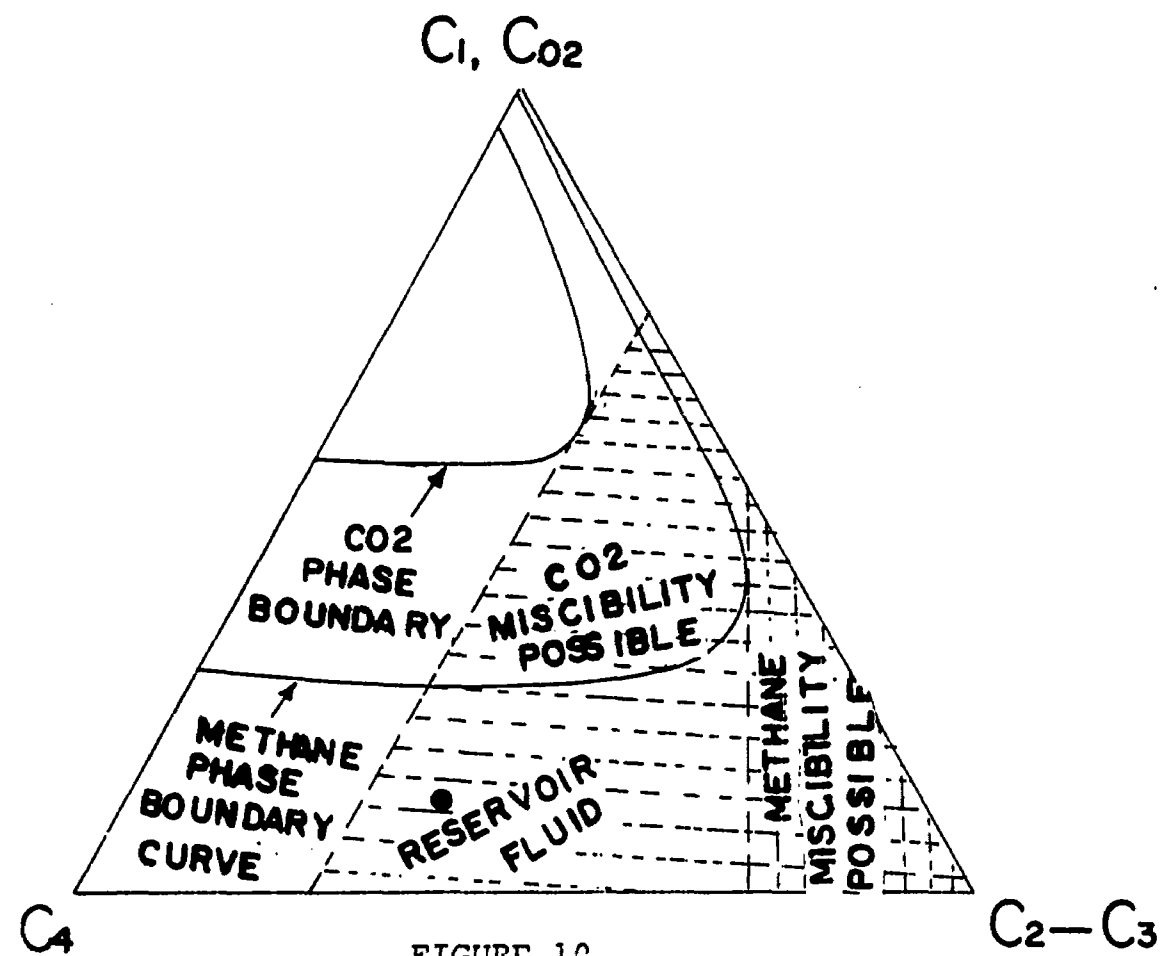


FIGURE 10.
 LABORATORY SIMULATION OF THE RESERVOIR
 HIGH PRESSURE CO₂ INJECTION

of the reservoir by the cell is assumed. Instead of injecting fresh carbon dioxide gas to push the gas available from first time of composition G_1 to contact the fresh surface of the oil as done in the reservoir, the carbon dioxide in the cell itself of composition G_1 obtained from the first shake at the injection pressure will contact the oil with more chance to touch all of its fresh parts by the second shake, and the gas will end up with an overall composition G_2 since it had more chance to pick up the light ends. This will result in a vapor phase composition G_2 and a liquid phase composition L_2 . The rocking of the cell for a short time will give C_2 , G_2 and L_2 , the overall, vapor, and liquid compositions, respectively. But rocking the cell continuously until the molecules of any component go into the vapor phase causes them to be in equilibrium with the other molecules of the same component in the liquid phase. In other words, rocking the cell allows those molecules to jump from the liquid phase to the vapor phase until an equilibrium is reached. There will be no more molecules moving from one phase to the other since the vapor pressures of any component in the liquid and in the vapor phase are in equilibrium. The oil should have a composition that could encourage the carbon dioxide to pick up some of the light ends at the equilibrium injection pressure; in other words, a composition below the bubble point curve in the ternary diagram and to the right of the line tangent to the critical point and parallel to the tie lines.

Physical Properties of Carbon Dioxide

The following properties will summarize the behavior of carbon dioxide injection into crude oil.

Effectiveness of Carbon Dioxide in Recovering Oil

The effectiveness of carbon dioxide in recovering oil has already been discussed in detail in Chapter II and shown in Figure 2. This was studied carefully by Whorton and Browncombe (45). Many other workers observed this behavior a long time ago (8, 24, 36, 40). Even the use of carbon dioxide was studied and indicated recently by References 39 and 44.

The Effect of the Size of the Gas Cap of Carbon Dioxide

This was investigated in detail by Dunegan (8) where he concluded that the larger the size of the gas cap, the more oil will be recovered. In his work he mentioned that at a pressure of 4000 psig almost 57 percent of the oil in place could be recovered if the size of the gas cap of carbon dioxide, M (ratio of reservoir gas volume to reservoir oil volume), is increased to 6.15 (see Figure 11).

Solubility of Carbon Dioxide in Crude Oil

This property was investigated by Beecher and Parkhurst (1). They indicated that carbon dioxide is far more soluble in crude oil under the same pressure and temperature than is natural gas. Figure 12 shows that the solubility of carbon dioxide in crude oil of 30.2 °API gravity is much more than the natural gas solubility in the same oil.

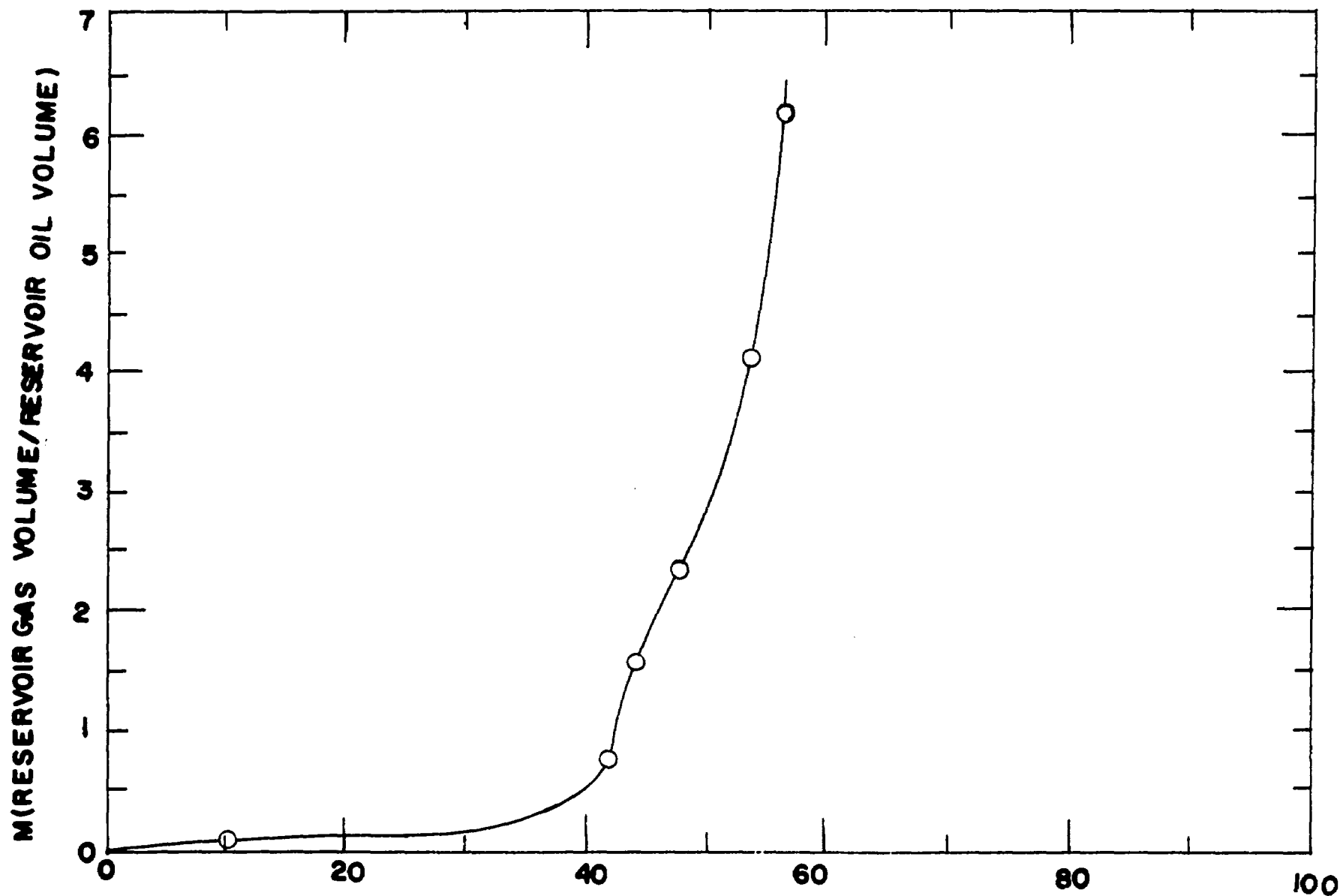


FIGURE 11. CONDENSATE RECOVERY % STO IN PLACE

M VS. CONDENSATE RECOVERY BY CO₂ AT PRESSURE 4000 PSIG
MODIFIED AFTER DUNEGAN.

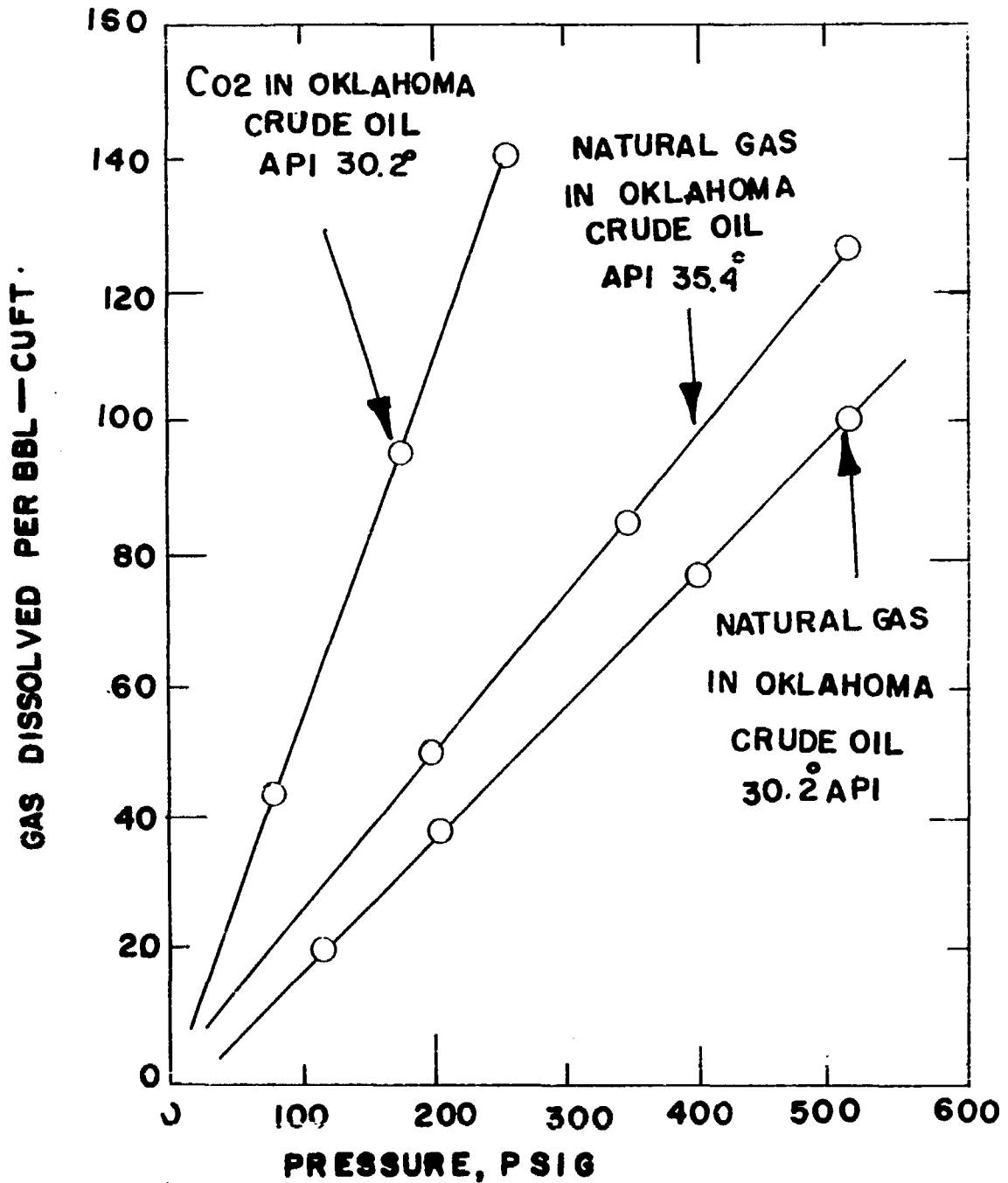


FIGURE 12. SOLUBILITY OF NATURAL GAS & CO₂ IN CRUDE OILS UNDER PRESSURE AT 70°F
 MODIFIED AFTER BEECHER AND PARHURST.

Reduction of Viscosity of Crude Oil by Carbon Dioxide under Pressure

This property was also investigated by Beecher and Parkhurst (1). They concluded that the reduction in viscosity of crude oil by carbon dioxide is much greater than that obtained by natural gas. Figure 13 is not quantitatively exact but is a qualitative figure. Viscosity reduction is a very important element in the fluid flow equation since reduction in the viscosity of the oil will cause the oil to flow faster.

Reduction of Surface Tension of Crude Oil by Carbon Dioxide

Carbon dioxide reduces the surface tension of the reservoir fluid. This is an important factor controlling the capillary forces which cause huge amounts of oil to be left in the reservoirs. These forces depend on the surface tension between the oil and the rock and between the water and the oil. Reduction of the surface tension between the wetting and nonwetting phases will reduce the capillary force. This is the pressure required to overcome the interfacial forces in between the reservoir fluids. This phenomenon was investigated by Swartz (40) (see Figure 14).

Vapor Pressure of Carbon Dioxide

The low value of vapor pressure of carbon dioxide is important for comparison only. The vapor pressure of carbon dioxide at 22.5°F is approximately 450 psig (42) while the

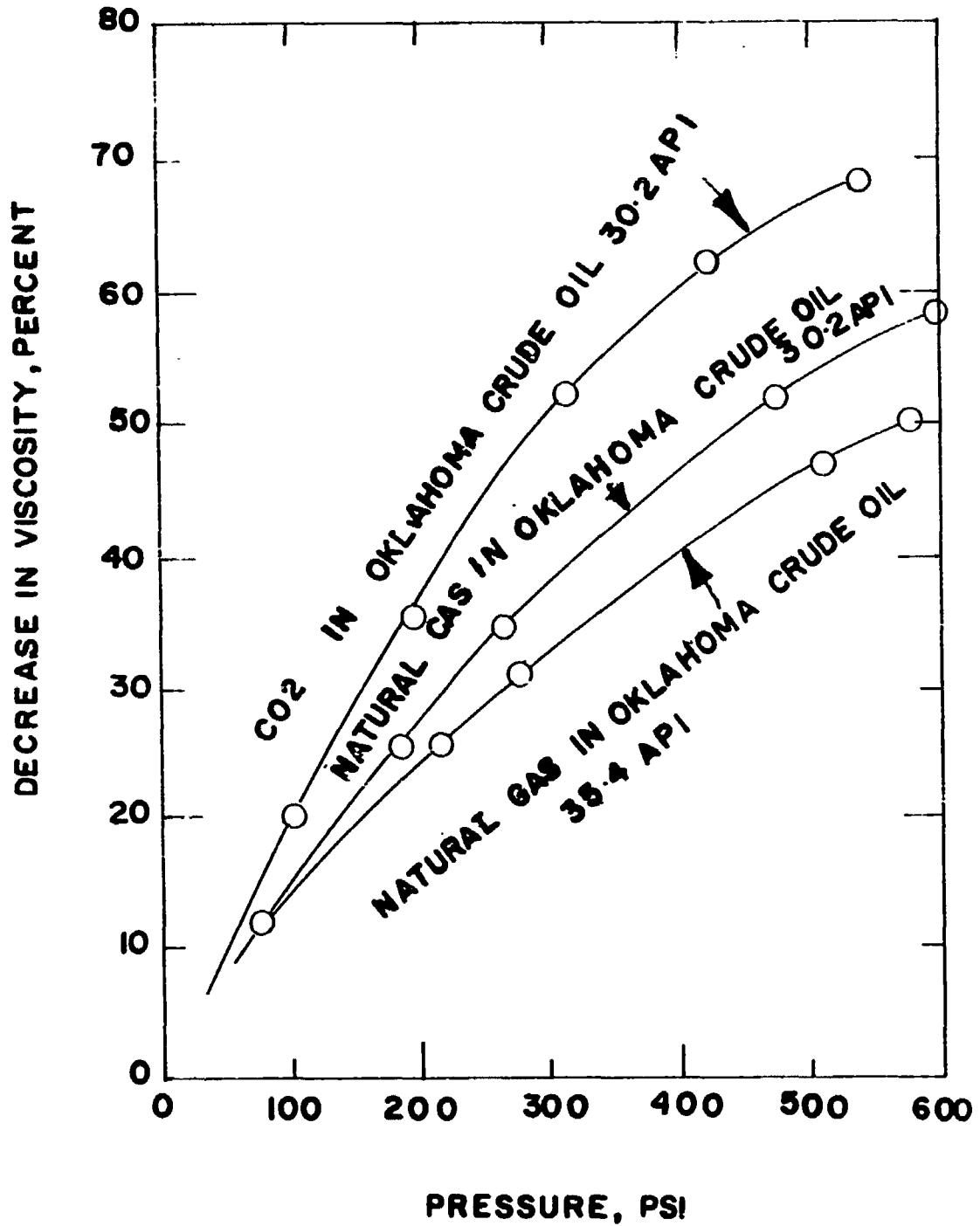
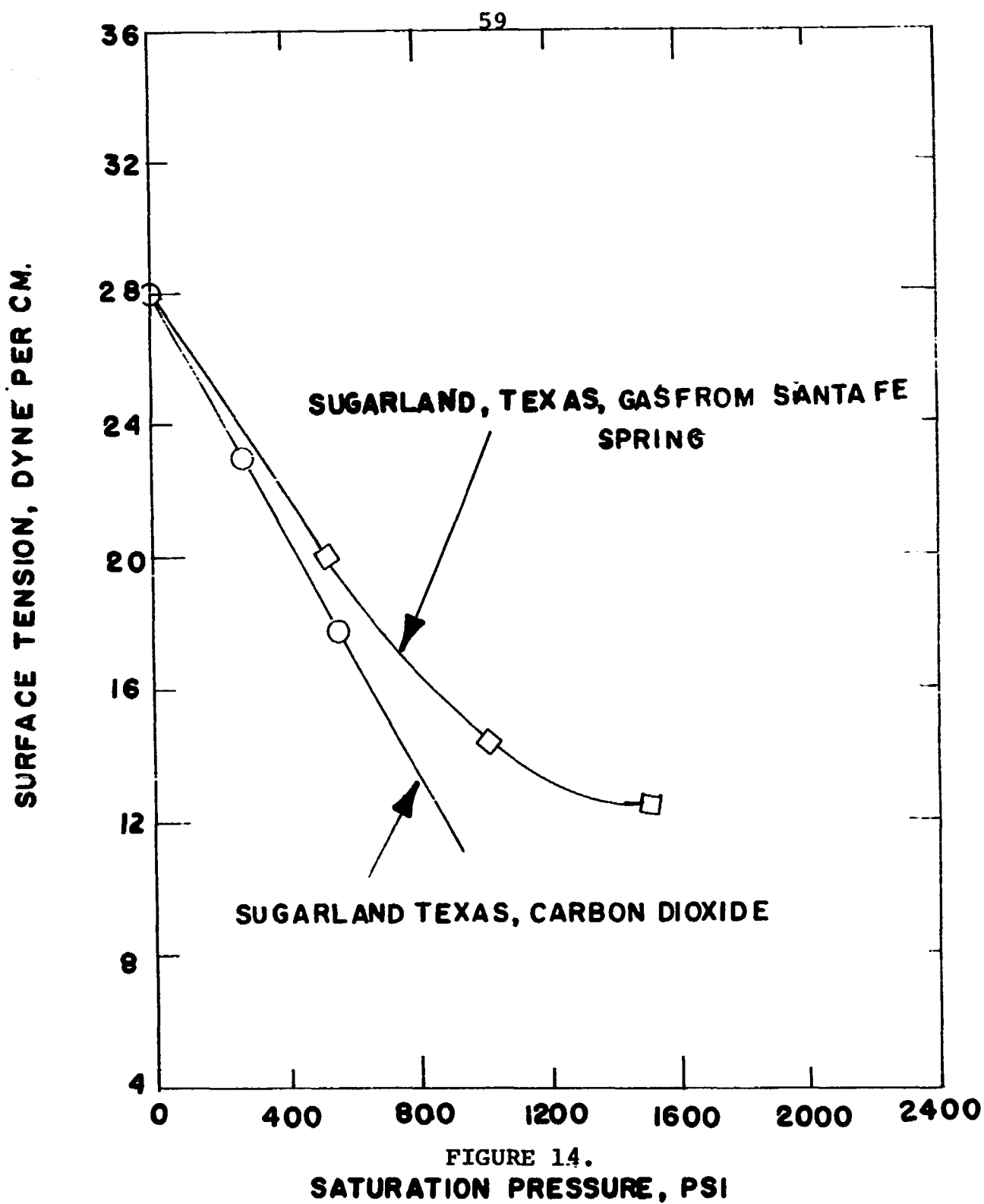


FIGURE 13.

**DECREASE IN VISCOSITY OF CRUDE OIL
CONTAINING GASES UNDER PRESSURE**

MODIFIED AFTER BEECHER AND
PARKHURST



**SURFACE TENSION OF CRUDE OIL
AS FUNCTION OF SATURATION PRESSURE
MODIFIED AFTER SWARTZ**

vapor pressure of methane at the same temperature is 3200 psig (18).

Thermodynamic Properties of Carbon Dioxide

Carbon dioxide can exist as a gas, liquid or solid. Figure 15 shows enthalpy versus temperature for a carbon dioxide system (7). The right hand side represents the gaseous region, the upper left hand side is the liquid region and the lower left represents the solid carbon dioxide region. The area under the curve represents the two phase region.

Miscellaneous Properties of Carbon Dioxide

Density at 34°F = 0.93, Reference (7)

Molecular weight = 44.01

Critical Pressure = 1073.0 psig

Critical temperature = 87.8°F

Compressibility of Mercury

The compressibility of mercury at 22°C (72°F) was obtained from Perry (Reference 34):

$$B_0 = \frac{1}{V_0} \frac{dv}{dp}$$

<u>Pressure</u> <u>mega bars</u>	<u>Compressibility/mega bars</u> <u>$B_0 \times 10^6$</u>
300	3.95
500	3.97
1000	3.91
12000	2.37

Note: 1 mega bar = 0.987 atm = 10^6 dyne/cm²

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The average compressibility of mercury at 102, 204, 306 mega bars (or approximately 1500, 3000, 4500 psig, the working pressures in these experiments) is assumed to be 4×10^{-6} cc/cc/mega bar.

Theoretical Calculation

An attempt was made to calculate theoretically the recovery of oil by carbon dioxide injection, but this attempt required a knowledge of certain variables. These variables are oil composition, molecular weight, specific gravity, K values of oil components, convergence pressure and the K values of carbon dioxide at the operating pressures. Composition, molecular weight and specific gravity of the oils were determined experimentally, and they are presented in the next chapter. Values for convergence pressure and K values were investigated theoretically since the K values depend on composition, pressure, temperature and convergence pressure. The temperature of the reservoir was 100°F and was constant.

A flash calculation program using the Newton Raphson method to find the roots of the modified flash equation was written to cover all four oils at all the operating pressures and at three different convergence pressures, but due to certain difficulties in obtaining the K values for the heavy components, specifically oil No. 2 and oil No. 4, the program was limited to calculations for oil No. 1 and oil No. 3 at all operating pressures, 4500, 3000, and 1500 psig and at

10,000 psig convergance pressure. The equilibrium flash vaporization calculations were limited to carbon dioxide and five oil components at 4500 psig and then to carbon dioxide and four oil components at 1500 and 3000 psig. This limitation was due to the unavailability of K values of the heavy oil components at the operating conditions in the experiments. But their theoretical estimates made it impossible for the system at the above conditions to reach equilibrium.

Methods to Find K Values

The K values are usually determined by one of the following methods (4, 38).

Dalton and Rault law: The simplest method to find K values is from Rault and Dalton's laws. Rault's law states that the partial pressure of a component is equal to the mole fraction of the component in the liquid phase multiplied by the vapor pressure of the pure component at the system temperature. Dalton's law states that the vapor pressure of a component in an ideal vapor is equal to the total pressure exerted by the vapor multiplied by the mole fraction of the component in the vapor.

$$PP_i = X_i P_i \text{ (Rault's law)}$$

$$PP_i = Y_i P \text{ (Dalton's law)}$$

where PP_i = partial presusre of i component in the vapor phase

X_i = mole fraction of the i component in the liquid phase

Y_i = mole fraction of the i component in the vapor phase

P_i = vapor pressure of the pure component at the system temperature

P = total pressure of the system

$$K_i = \frac{Y_i}{X_i} = \frac{P_i}{P}$$

In an attempt to estimate the K values of the other components which are $C_{10}H_{22}$ up to $C_{16}H_{34}$, a straight line plot of K values versus P_i on log-log paper was adopted according to the following equation:

$$\log K_i = \log P_i - \log P$$

Some of the components of known K values were plotted, and then the vapor pressures of the heavy components at the system temperature 100°F were found by extrapolation (18). These were compared with those obtained by the Antoine equation method (37) and showed good agreement. Next, an extrapolation of a straight line plotted using these values of vapor pressure enabled the K values for each component $C_{10}H_{22}$ to $C_{16}H_{34}$ to be obtained. However, there was a limitation to this method since the above straight line plot is for an ideal gas law. A pure component has no vapor pressure at a temperature above its critical temperature. For practical purposes the ideal gas law assumption will hold only to a pressure of 50 to 100 psig (38) and others claim that the system pressure should be less than 50 psig (References 4 and 37). The minimum

experimental pressure was 1500 psig and the temperature was 100°F.

Fugacity method: The second method to find the K values is the fugacity method.

$$f_i^{-L} = X_i f_i^L$$

$$f_i^{-V} = Y_i f_i^V$$

i = component identity index

f_i^{-} = fugacity of component i in the mixture

V = superscript, vapor phase identity index

L = superscript, liquid phase identity index

X_i = mole fraction, concentration of component i in the liquid phase

Y_i = mole fraction, concentration of component i in the vapor phase

f_i = fugacity of component i in the pure liquid or vapor state at the system temperature and pressure

At equilibrium

$$f_i^{-L} = f_i^{-V}$$

thus,
$$X_i f_i^L = Y_i f_i^V$$

$$K_i = \frac{Y_i}{X_i} = \frac{f_i^L}{f_i^V}$$

These are ideal K values based on the assumption that the mixture is volume additive, i.e., it is ideal. These K values can be used only up to a pressure of 300 psig (38) although other investigators claim they can be used up to 500 psig.

BWR method: K values are determined by using the BWR equation of state to determine the P-V-T-X relationship of a non-ideal solution (3). Direct calculation of K values from such an equation is accurate (4), but time consuming (38). Also, it is only for light hydrocarbons.

Correlated experimental K values method: Correlation of experimental K values are based on a compilation of actual data obtained from field separations and from the laboratory for gas-crude oil systems. These K values should be used below 1000-1200 psig (4). The K values of a real system are a function of pressure, temperature and composition.

Heaviest fraction method: This method used to find the K values of the heaviest fraction in the system is discussed in detail in References 4 and 16.

Empirical equation method: A formula developed recently by Canfield (5) finds the K values for some of the oil components by utilizing certain data such as working pressure, convergence pressure, system temperature, critical temperatures of the oil components and critical compressibility factor of the components.

The empirical formula is

$$K_i = (1/PR) \exp [Q_i R_i (1 - PR)^{(0.33/TR_i)}]$$

$$Q_i = 10.7016 - \ln (P_{\text{conv}}) - 4.4316/TR_i - 0.1968/(TR_i)^3$$

$$R_i = 6.3816 - 29.0020 (Z C_i) + 35.3443 (Z C_i)^2$$

where K_i = K value of the i component in a mixture, equilibrium constant = Y_i/X_i

PR = system pressure ratio equal to system pressure in psig divided by the convergence pressure of the mixture in psig

TR = temperature ratio of the i component equal to the temperature of the system in degrees Rankine divided by the critical temperature of the component in degrees Rankine

$Z C_i$ = critical compressibility factor of component i

A program was written to evaluate these K values at convergence pressures from 6000 to 11000 with an increment of 1000 psig for this system, which consists of carbon dioxide and four or five oil components. This program is presented in Table 3. Its results are presented in Table 4.

Convergence pressure method: This is the most common approach (4) to estimate the K values based on the variables, temperature, working pressure, convergence pressure and composition of the oil. The convergence pressure is that pressure at which the K value of each component in the system converges to one. In this method, a value of convergence pressure is estimated, the K values are obtained, and then flash calculations are performed. The liquid phase composition is divided into two parts to form a pseudo binary system. One part is the light component, methane, and the other part represents all components except methane. The critical temperature of the second part is calculated by:

TABLE 3

METHOD OF CALCULATION OF THE K VALUES BY
THE EMPIRICAL EQUATION

```

$JOB      450929986.KP=29
C      CALCULATION OF THE K VALUES
1      DIMENSION TC(7),ZC(7),AK(7)
2      T=100.
3      N=7
4      READ(5,51)(TC(I),I=1,N)
5      READ(5,51)(ZC(I),I=1,N)
6      51  FORMAT(7F10.5)
7      PCCN=5000.
8      DO 550 KK=1,6
9      P=4500.
10     II=1
11     PCCN=PCCN+1000.
12     55  WRITE(6,61)P
13     WRITE(6,69) PCON
14     69  FORMAT(5X,'PCON='F10.3)
15     61  FORMAT(//,5X,'THE WORKING      PRESSURE IS='F10.5)
16     WRITE(6,62)(I,TC(I),I,ZC(I),I=1,N)
17     62  FORMAT(5X,'TC(',I1,')='F10.5,5X,'ZC(',I1,')='F10.5)
18     DO 64 I=1,N
19     PR=P/PCON
20     TR=(T+460.)/TC(I)
21     Q=10.7016-ALOG(PCCN)-4.4316/TR-0.19680/(TR**3)
22     R=6.3816-29.002*(ZC(I))+35.3443*(ZC(I)**2)
23     F=0.33/TR
24     AK(I)=(1./PR)*EXP(Q*R*(1.-PR)**F)
25     64  CONTINUE
26     WRITE(6,65)(I,AK(I),I=1,N)
27     65  FORMAT(//,5X,'AK(',I2,')='F10.5)
28     II=II+1
29     IF(II-3)52,53,550
30     52  P=3000.
31     GO TC 55
32     53  P=1500.
33     GO TC 55
34     550  CONTINUE
35     STCP
36     END

```

```

THE WORKING      PRESSURE IS=4500.00000
PCCN=  6000.000
TC(1)=  343.30000      ZC(1)=   0.29000
TC(2)=  549.77000      ZC(2)=   0.28800
TC(3)=  665.94990      ZC(3)=   0.27800
TC(4)=  765.31000      ZC(4)=   0.27400
TC(5)=  845.60000      ZC(5)=   0.26800
TC(6)=  914.10000      ZC(6)=   0.26400
TC(7)=  547.80000      ZC(7)=   0.27600

```

TABLE 4

K VALUES OBTAINED FROM THE EMPIRICAL EQUATION

		Oil Components					
		C_1H_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CO_2
Convergence pressure = 6000							
Working pressure:	4500	0.7757	0.2819	0.1486	0.0938	0.06085	0.2386
	3000	1.0724	0.2859	0.1122	0.0531	0.0255	0.2324
	1500	2.033	0.4352	0.1366	0.0513	0.0192	0.3441
Convergence pressure = 7000							
Working pressure:	4500	0.7722	0.2445	0.1180	0.0620	0.035	0.2005
	3000	1.080	0.2705	0.0984	0.0434	0.0193	0.2150
	1500	2.05248	0.4281	0.1292	0.0469	0.01693	0.3321
Convergence pressure = 8000							
Working pressure:	4500	0.7704	0.2234	0.0929	0.0470	0.0242	0.0139
	3000	1.0855	0.2599	0.0894	0.0374	0.0157	0.2026
	1500	2.0672	0.4228	0.1237	0.0438	0.0153	0.3226
Convergence pressure = 9000							
Working pressure:	4500	0.7691	0.2095	0.0811	0.0385	0.0184	0.1643
	3000	1.0894	0.2520	0.0830	0.0334	0.0134	0.1930
	1500	2.0793	0.4187	0.1195	0.0414	0.0142	0.3150

TABLE 4--Continued

		Oil Components					
		C_1H_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	CO_2
Convergence pressure = 10,000							
Working pressure:	4500	0.7681	0.1995	0.0731	0.0329	0.0149	0.1539
	3000	1.0925	0.2460	0.0781	0.0304	0.0118	0.1860
	1500	2.0895	0.4154	0.1160	0.03959	0.0132	0.3086
Convergence pressure = 11,000							
Working pressure:	4500	0.7672	0.1919	0.0672	0.0290	0.0125	0.1459
	3000	1.0951	0.2412	0.0743	0.0282	0.0106	0.1800
	1500	2.0980	0.4128	0.1132	0.0381	0.0125	0.3032

$$T_{ch} = \frac{\sum_{i=2}^{7+} X_i M_i T_{ci}}{\sum_{i=2}^{7+} X_i M_i}$$

where X_i = mole fraction of i^{th} component in the liquid phase

M_i = molecular weight of the i^{th} component

T_{ci} = critical temperature of the i^{th} component

T_{ch} = critical temperature of the second part of the pseudo binary system, i.e., the weighted average equilibrium temperature

Then referring to Figure 3 of Reference 29, there is a plot of convergence pressure versus the critical temperature for the lightest components such as methane, and also for the remaining pseudo heavy part. The convergence pressure can be read from this chart. If the obtained convergence pressure value is not close enough to the assumed one, then a second guess of a convergence pressure is required, and the above process of calculation will be repeated until the convergence pressure obtained from the chart equals the assumed convergence pressure.

There is another method to calculate the convergence pressure. It is an empirical equation suggested by E. I. Organick, et al. (33):

$$\log P_K = A + BT + CT^2 + E/T$$

$$\begin{aligned} \text{where } A &= A_0 + A_1 T_{ch} + A_2 T_{ch}^2 + A_3 T_{ch}^3 \\ B &= B_0 + B_1 T_{ch} + B_2 T_{ch}^2 + B_3 T_{ch}^3 \end{aligned}$$

$$C = C_0 + C_1 T_{ch} + C_2 T_{ch}^2 + C_3 T_{ch}^3$$

$$E = E_0 + E_1 T_{ch} + E_2 T_{ch}^2 + E_3 T_{ch}^3$$

The values of the above sixteen constants are given in Reference 33.

T = temperature of the system, °F

T_{ch} = equilibrium temperature of the system

P_K = convergence pressure in psig

In this method the K values are selected at an assumed convergence pressure and a flash calculation is performed. Then the liquid composition obtained at the equilibrium is used to calculate the equilibrium critical temperature of the system (T_{ch}) in a manner similar to the convergence pressure method. The convergence pressure is next calculated using the value of the system critical temperature, T_{ch} , and the previous equation. If the convergence pressure obtained is not equal to that which was assumed, then another convergence pressure will be assumed and other K values will be obtained and a new T_{ch} will be calculated until the convergence pressure calculated is close to the assumed value. A computer program was written to find the convergence pressure using this empirical equation, but no encouraging results were obtained. Hence this method was not used. However, the program is presented in Table 5.

A flash calculation program using the Newton Raphson method to find the roots of an equation was written. This program was derived from the first fundamental equations of

TABLE 5

METHOD OF CALCULATION OF CONVERGENCE PRESSURE

```

SJOB          450929986.KP=29
C      CALCULATION OF THE CONVERGENCE PRESSURE
1      DIMENSION A(4),B(4),C(4),E(4),TC(9),EM(9),X(9)
2      READ (5,51)(A(I),I=1,4)
3      READ(5,51)(B(I),I=1,4)
4      READ(5,51)(C(I),I=1,4)
5      READ(5,51)(E(I),I=1,4)
6      N=9
7      READ(5,52)(EM(I),I=1,N)
8      READ(5,52)(TC(I),I=1,N)
9      READ(5,53)(X(I),I=1,N)
10     53  FORMAT(8F10.5)
11     51  FORMAT(4E20.8)
12     52  FORMAT(8F10.3)
13     N=9
14     DO 54 I=1,N
15         TC(I)=TC(I)-460.
16     54  CONTINUE
17     N=9
18     SSUMN=0.0
19     SSUMD=0.0
20     DO 10 I=1,N
21         SSUMN=SSUMN+X(I)*EM(I)*TC(I)
22         SSUMD=SSUMD+X(I)*EM(I)
23     10  CONTINUE
24     TCH=SSUMN/SSUMD
25     AA=A(1)+A(2)*TCH+A(3)*TCH**2+A(4)*TCH**3
26     BB=B(1)+B(2)*TCH+B(3)*TCH**2+B(4)*TCH**3
27     CC=C(1)+C(2)*TCH+C(3)*TCH**2+C(4)*TCH**3
28     EE=E(1)+E(2)*TCH+E(3)*TCH**2+E(4)*TCH**3
29     T=100.
30     F=AA+BB*T+CC*T**2+EE/T
31     PK=2.303*EXP(F)
32     WRITE(6,61)PK
33     61  FORMAT(5X,'THE CONVERGENCE PRESSURE IS PK=',F15.5)
34     STOP
35     END

```

SEXEC

flash equilibrium vaporization. The program was written for a mixture of carbon dioxide and four or five other oil components including the heavy components, the four components being the heavy oil components for 1500, 3000 psig and five components being the heavy oil components for 4500 psig. This program was used for a temperature of 100°F and a convergence pressure of 10,000 psig for oil No. 1 and oil No. 3. Equilibrium means there is no change in the composition of the vapor and the liquid in contact with each other (4). In other words the rates of vaporization and condensation of a given molecular species are equal so that no net change in composition occurs.

Flash Calculation Principles

Material balance equation:

N = total number of moles fed into the system

Y_i = mole fraction of i component in the vapor phase

X_i = mole fraction of i component in the liquid phase

V = total number of moles of the vapor at the equilibrium

L = total number of moles of the liquid

Z_i = mole fraction of i component in the feed

Assume:

$N = 1$ mole

$Z_i \cdot 1 = (Y_i V) + (L X_i)$

$K_i = Y_i / X_i$ at equilibrium

$1 = L + V$

$$Z_i = K_i X_i V + L X_i$$

$$\begin{aligned} Z_i &= K_i X_i V + (1 - V) X_i \\ &= K_i X_i V + X_i - X_i V \\ &= V X_i (K_i - 1) + X_i \end{aligned}$$

$$Z_i = X_i [V(K_i - 1) + 1]$$

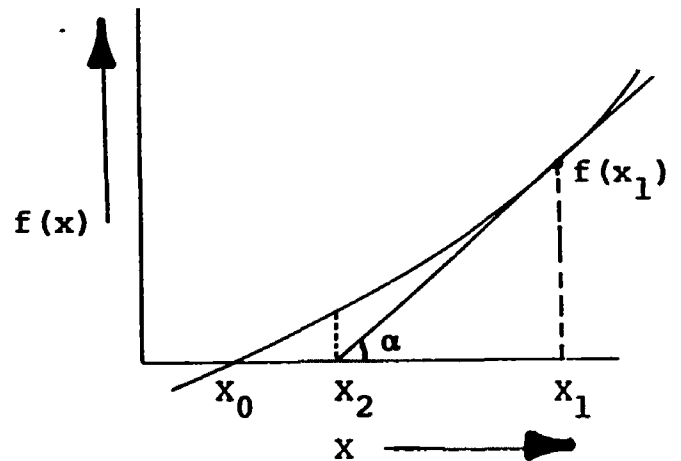
$$X_i = \frac{Z_i}{V(K_i - 1) + 1}$$

$$\sum X_i = 1$$

$$\sum Y_i = 1$$

$$Y_i = \frac{K_i Z_i}{V(K_i - 1) + 1}$$

A method of calculation to find V and L utilizing the Newton Raphson method instead of the trial and error method is developed as follows:



$$\sum Y_i - \sum X_i = 0$$

$$\tan \alpha = \frac{f(x_1)}{x_1 - x_2}$$

$$f'(x_1) = \frac{f(x_1)}{x_1 - x_2}$$

$$x_1 - x_2 = \frac{f(x_1)}{f'(x_1)}$$

$$x_2 = x_1 - \frac{f(x_1)}{f'(x_1)}$$

$$f(V) = \sum Y_i - \sum X_i$$

$$= \frac{K_i Z_i}{V(K_i - 1) + 1} - \frac{Z_i}{V(K_i - 1) + 1}$$

$$f(V) = \frac{Z_i (K_i - 1)}{V(K_i - 1) + 1}$$

$$f'(V) = \frac{-Z_i (K_i - 1) (K_i - 1)}{[V(K_i - 1) + 1]^2}$$

$$V_{ii+1} = V_{ii} - \frac{f(V)}{f'(V)}$$

$$= V_{ii} + \frac{\sum \frac{Z_i (K_i - 1)}{V_{ii}(K_i - 1) + 1}}{\sum \frac{Z_i (K_i - 1)^2}{[V_{ii}(K_i - 1) + 1]^2}}$$

CHAPTER VI

PRESENTATION AND DISCUSSION OF THE RESULTS

The primary objective of this study was to find the effect of gravity and pressure on oil recovery by high pressure carbon dioxide injection. It was discovered that the oil composition plays an important role in controlling oil recovery. The objectives were established experimentally and then theoretically.

Several types of experiments were required in this investigation. They covered evaporation and condensation, specific gravity, molecular weight and chromatograph and mass spectrometer analyses. Also, a computer program to support the theoretical investigation was composed. Results for each group are presented and discussed separately. However, results from all the experimental groups are brought together in the discussion of the objectives.

Much work was done to obtain a mathematical formula which could predict the volume of carbon dioxide injected at equilibrium pressure for a given quantity of oil resulting in the same gas cap size in all the experiments. This was attempted by using certain thermodynamic properties of carbon dioxide, the solution gas-oil ratio, the formation volume

factor obtained from Reference 25, and the compressibility of carbon dioxide obtained from Reference 19 and presented in Figure 16. These were used with a constant oil volume. However these data did not give exactly the same size of the gas cap in the first two experimental runs. This might be expected since the data obtained from Reference 25 were established for an oil different from those used in the present investigation. It was of different gravity and of different composition. Even the experimental conditions were different. A pure judgement as to a good guess based on the previous experimental results was applied. Some of the experiments took two weeks to perform, and others took four weeks, depending on the viscosity and gravity of the oil. The heavier the oil the longer the time required.

Twelve experiments were carried out, three experiments for each oil. A constant oil volume of 275 cc was injected for each run which was carried out at a constant temperature of 100°F. The other data and results of these experiments are presented in Table 6 through 17. Each of these tables represents a run for equilibrium pressures of 1500, 3000, and 4500 psig, respectively. Usually the lower equilibrium pressure experiment was carried out first. The volume of the carbon dioxide injected was recorded in these tables.

The oil recovered (condensate) from each run at equilibrium pressure was plotted as condensate recovered versus equilibrium pressure. Figures 17, 18, 19 and 20 represent

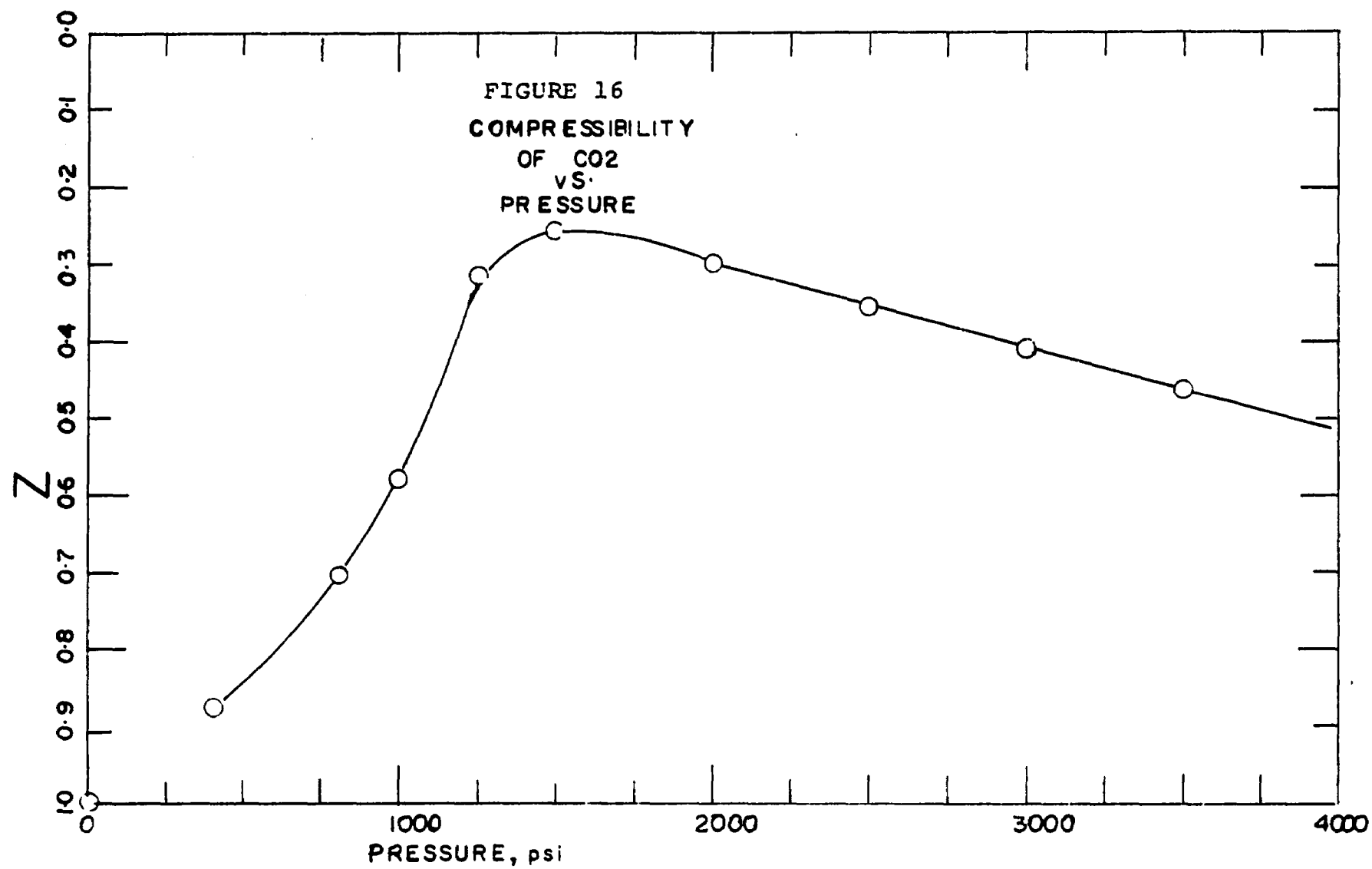


TABLE 6

SUMMARY OF EXPERIMENT NO. 1

Oil No. 1 (30.2 °API), Pressure C (1500 psig)

Oil gravity, °API	30.2
Equilibrium pressure, psig	1500.0
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	660.356
Volume of the oil sample at STC, cc	275.00
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	275.00
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	203.039
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	227.661
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 1500 psig, cc	5.242
Volume of the gas cap at equilibrium pressure and 100°F, cc	167.100
Volume of the gas produced, measured at STC, cuft	0.7213
Time duration required for condensation, sec	8,078
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	11.00
Volume of residual oil recovered, cc	262
B _o , Res. BBL/STB	1.250
Date of the experiment	1-7-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	11.00

TABLE 7

SUMMARY OF EXPERIMENT NO. 2

Oil No. 1 (30.2 °API), Pressure B (3000 psig)

Oil gravity, °API	30.2
Equilibrium pressure, psig	3000.0
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	670.016
Volume of the oil sample at STC, cc	275.00
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	280.776
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	280.639
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	300.846
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 3000 psig, cc	30.482
Volume of the gas cap at equilibrium pressure and 100°F, cc	238.083
Volume of the gas produced, measured at STC, cuft	1.7813
Time duration required for condensation, sec	9500
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	34.5
Volume of residual oil recovered, cc	238
B _O , Res. BBL/STB	1.303
Date of the experiment	7-14-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	24.2

TABLE 8

SUMMARY OF EXPERIMENT NO. 3

Oil No. 1 (30.2 °API), Pressure A (4500 psig)

Oil gravity, °API	30.2
Equilibrium pressure, psig	4500
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	666.093
Volume of the oil sample at STC, cc	275.0
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	281.923
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	224.106
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	257.682
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 4500 psig, cc	39.775
Volume of the gas cap at equilibrium pressure and 100°F, cc	173.643
Volume of the gas produced, measured at STC, cuft	2.0587
Time duration required for condensation, sec	17,910
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc to 4500 psig	32.00
Volume of residual oil recovered, cc	240
B _o , Res. BBL/STB	1.345
Date of the experiment	8-24-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	30.82

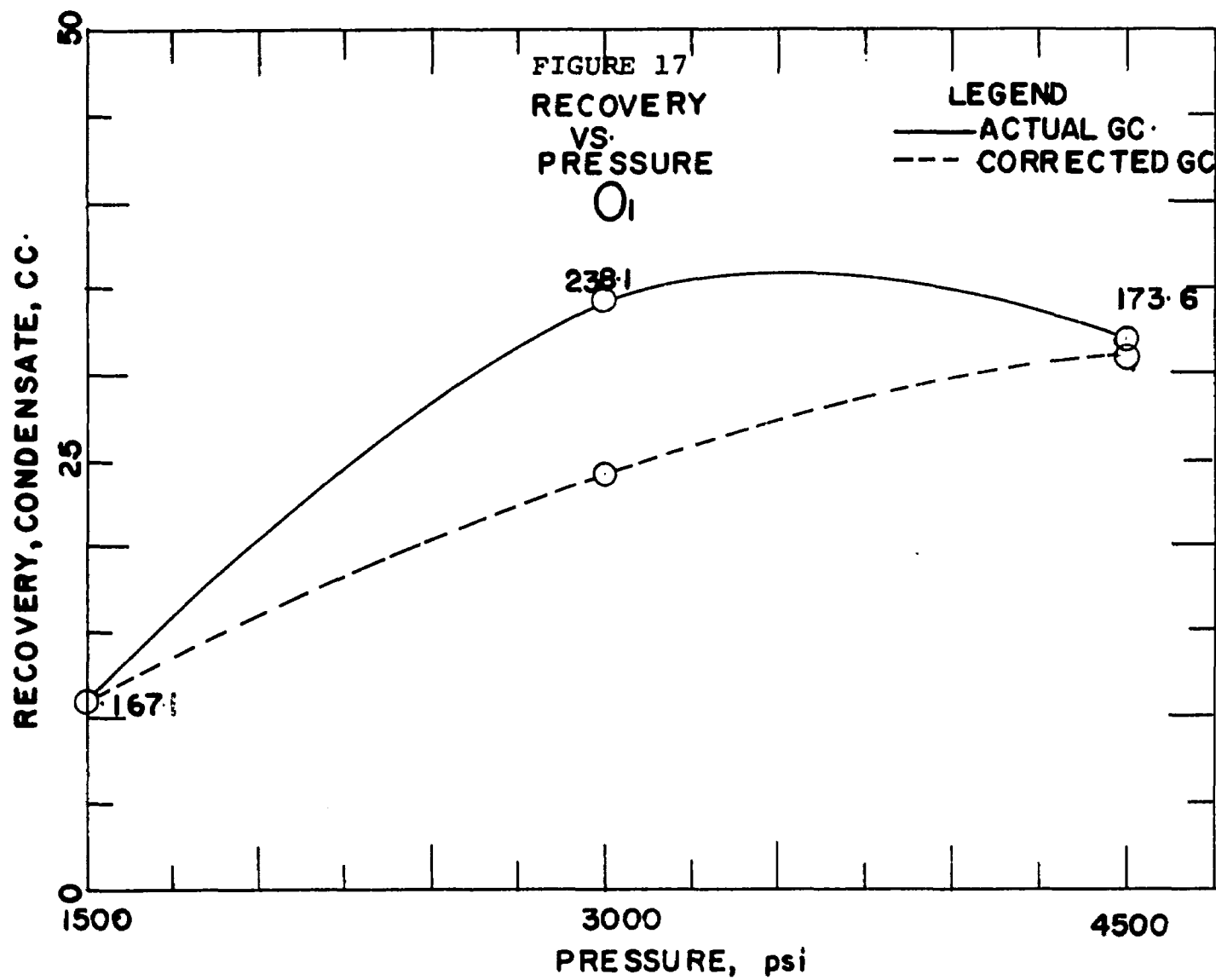


TABLE 9

SUMMARY OF EXPERIMENT NO. 4

Oil No. 2 (24.3 °API), Pressure C (1500 psig)

Oil gravity, °API	24.3
Equilibrium pressure, psig	1500
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	665.935
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	275.730
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	203.290
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	221.965
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 1500 psig, cc	5.883
Volume of the gas cap at equilibrium pressure and 100°F, cc	164.698
Volume of the gas produced, measured at STC, cuft	2.2628
Time duration required for condensation, sec	14,015
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	5.7
Volume of residual oil recovered, cc	269
B _O , Res. BBL/STB	1.212
Date of the experiment	7-29-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	5.80

TABLE 10

SUMMARY OF EXPERIMENT NO. 5

Oil No. 2 (24.3 °API), Pressure B (3000 psig)

Oil gravity, °API	24.3
Equilibrium pressure, psig	3000
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	699.596
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	279.633
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	250.602
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	279.823
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 3000 psig, cc	28.448
Volume of the gas cap at equilibrium pressure and 100°F, cc	207.007
Volume of the gas produced, measured at STC, cuft.	3.2124
Time duration required for condensation, sec	16,150
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	11.2
Volume of residual oil recovered, cc	262.5
B _o , Res. BBL/STB	1.232
Date of the experiment	9-8-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	9.05

TABLE 11

SUMMARY OF EXPERIMENT NO. 6

Oil No. 2 (24.3 °API), Pressure A (4500 psig)

Oil gravity, °API	24.3
Equilibrium pressure, psig	4500
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	667.751
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	294.00
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	221.166
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	250.311
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 4500 psig, cc	37.763
Volume of the gas cap at equilibrium pressure and 100°F, cc	173.0
Volume of the gas produced, measured at STC, cuft	1.9015
Time duration required for condensation, sec	13,643
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	12.50
Volume of residual oil recovered, cc	248
B _o , Res. BBL/STB	1.268
Date of the experiment	9-2-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	12.06

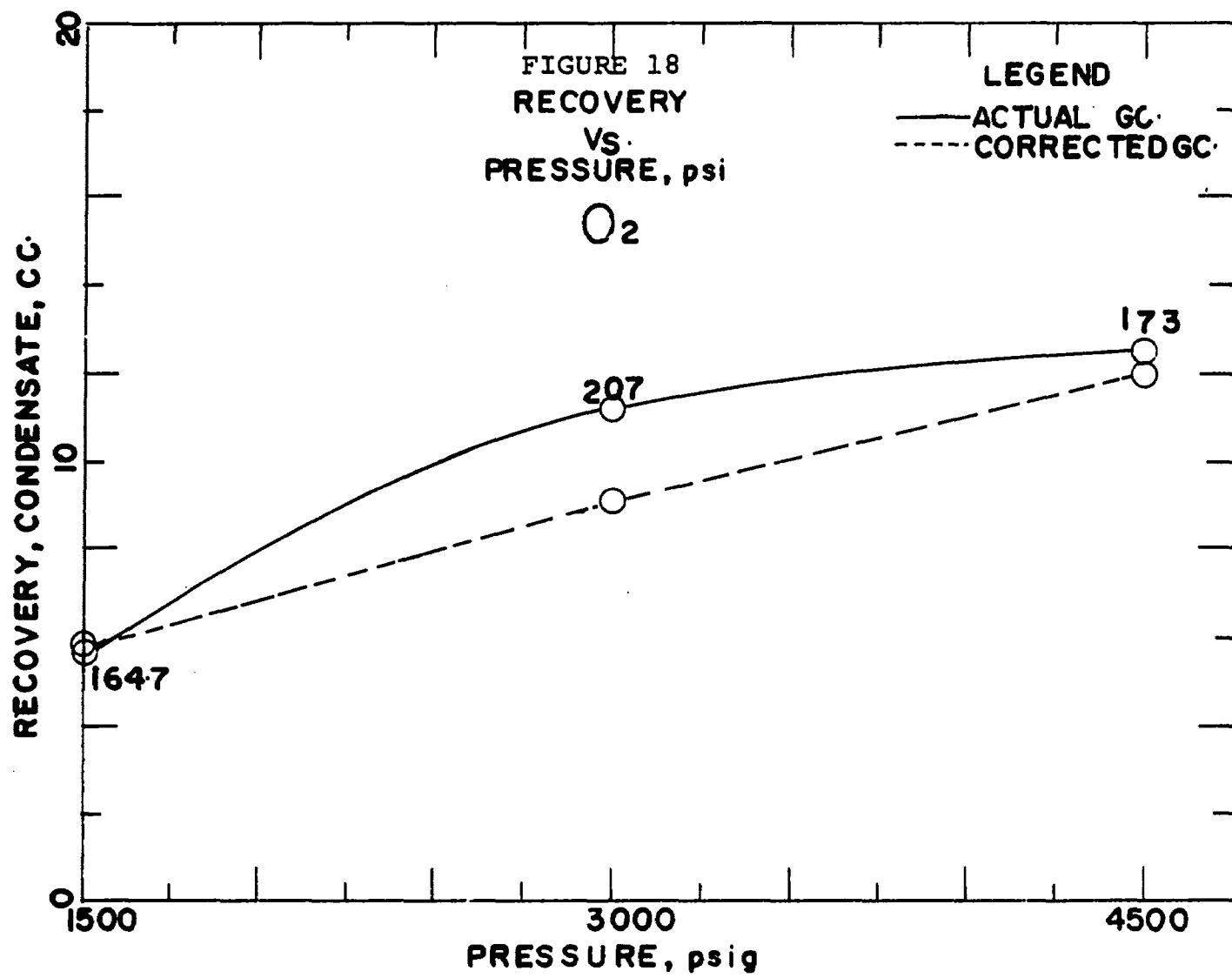


TABLE 12

SUMMARY OF EXPERIMENT NO. 7

Oil No. 3 (22.7 °API), Pressure C (1500 psig)

Oil gravity, °API	22.7
Equilibrium pressure, psig	1500
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	659.195
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	279.679
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	191.693
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	217.290
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 1500 psig, cc	3.278
Volume of the gas cap at equilibrium pressure and 100°F, cc	167.381
Volume of the gas produced, measured at STC, cuft	0.7452
Time duration required for condensation, sec	19,600
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	6.8
Volume of residual oil recovered, cc	268
B _o , Res. BBL/STB	1.218
Date of the experiment	8-13-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	6.8

TABLE 13

SUMMARY OF EXPERIMENT NO. 8

Oil No. 3 (22.7 °API), Pressure B (3000 psig)

Oil gravity, °API	22.7
Equilibrium pressure, psig	3000
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	666.482
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	281.719
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	206.339
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	261.255
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 3000 psig, cc	23.708
Volume of the gas cap at equilibrium pressure and 100°F, cc	190.790
Volume of the gas produced, measured at STC, cuft	1.8610
Time duration required for condensation, sec	33,358
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	13.7
Volume of residual oil recovered, cc	261.3
B _O , Res. BBL/STB	1.257
Date of the experiment	4-8-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	12.01

TABLE 14

SUMMARY OF EXPERIMENT NO. 9

Oil No. 3 (22.7 °API), Pressure A (4500 psig)

Oil gravity, °API	22.7
Equilibrium pressure, psig	4500
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	660.356
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	289.530
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	200.923
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	234.060
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 4500 psig, cc	38.240
Volume of the gas cap at equilibrium pressure and 100°F, cc	154.037
Volume of the gas produced, measured at STC, cuft	1.3485
Time duration required for condensation, sec	10,931.
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	14.5
Volume of residual oil recovered, cc	253
B _o , Res. BBL/STB	1.271
Date of the experiment	9-22-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	15.72

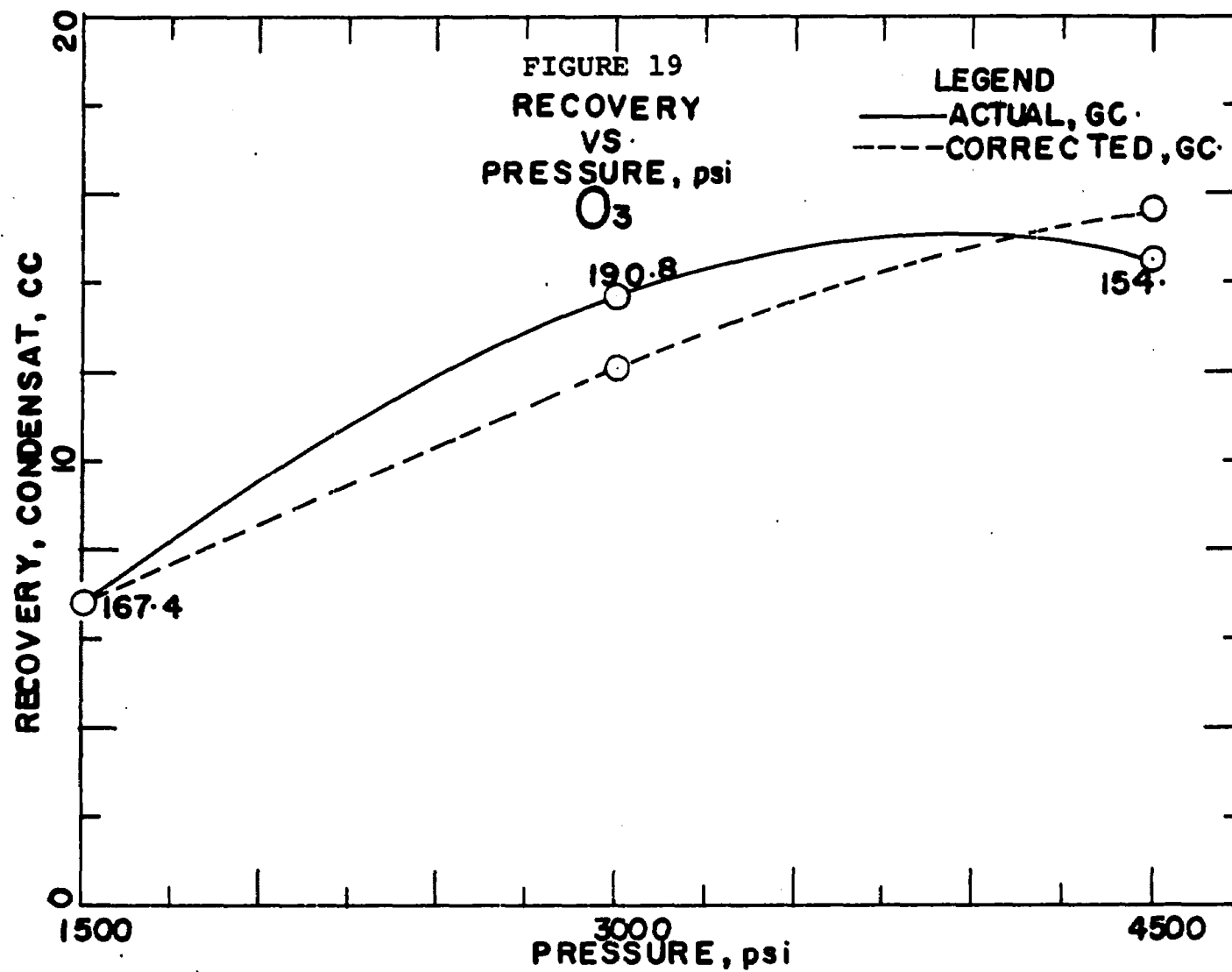


TABLE 15

SUMMARY OF EXPERIMENT NO. 10

Oil No. 4 (15.4 °API), Pressure C (1500 psig)

Oil gravity, °API	15.4
Equilibrium pressure, psig	1500
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	665.081
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	276.276
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	208.225
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	236.388
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 1500 psig, cc	3.7
Volume of the gas cap at equilibrium pressure and 100°F, cc	190.0
Volume of the gas produced, measured at STC, cuft	2.4055
Time duration required for condensation, sec	10,190
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	2.1
Volume of residual oil recovered, cc	264
B _O , Res. BBL/STB	1.17
Date of the experiment	10-20-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	1.85

TABLE 16

SUMMARY OF EXPERIMENT NO. 11

Oil No. 4 (15.4 °API), Pressure B (3000 psig)

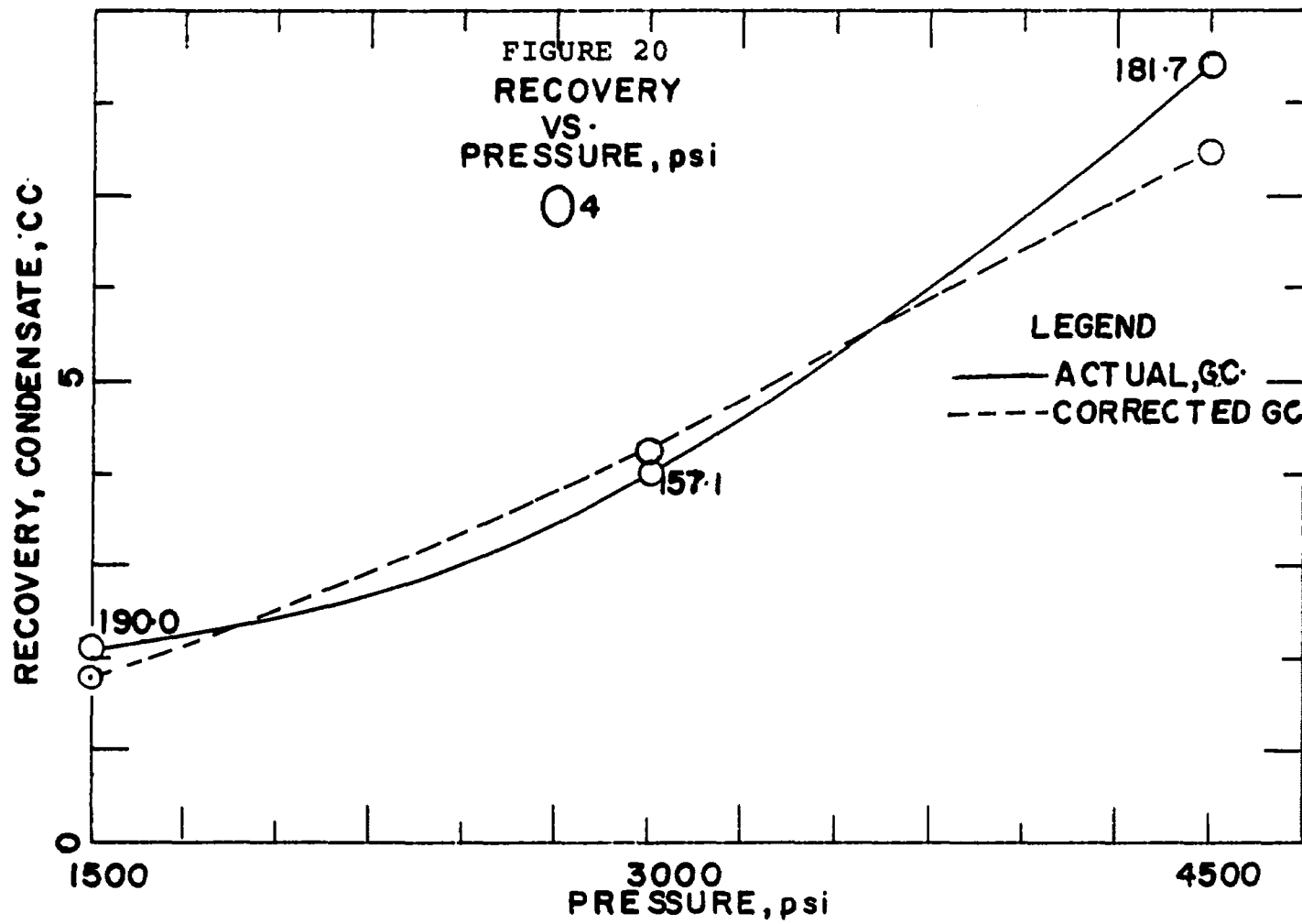
Oil gravity, °API	15.4
Equilibrium pressure, psig	3000
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	668.955
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	285.829
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	197.165
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	233.716
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 3000 psig, cc	30.163
Volume of the gas cap at equilibrium pressure and 100°F, cc	157.1
Volume of the gas produced, measured at STC, cuft	1.9983
Time duration required for condensation, sec	16,770
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	4.00
Volume of residual oil recovered, cc	271
B _o , Res. BBL/STB	1.226
Date of the experiment	10-8-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	4.25

TABLE 17

SUMMARY OF EXPERIMENT NO. 12

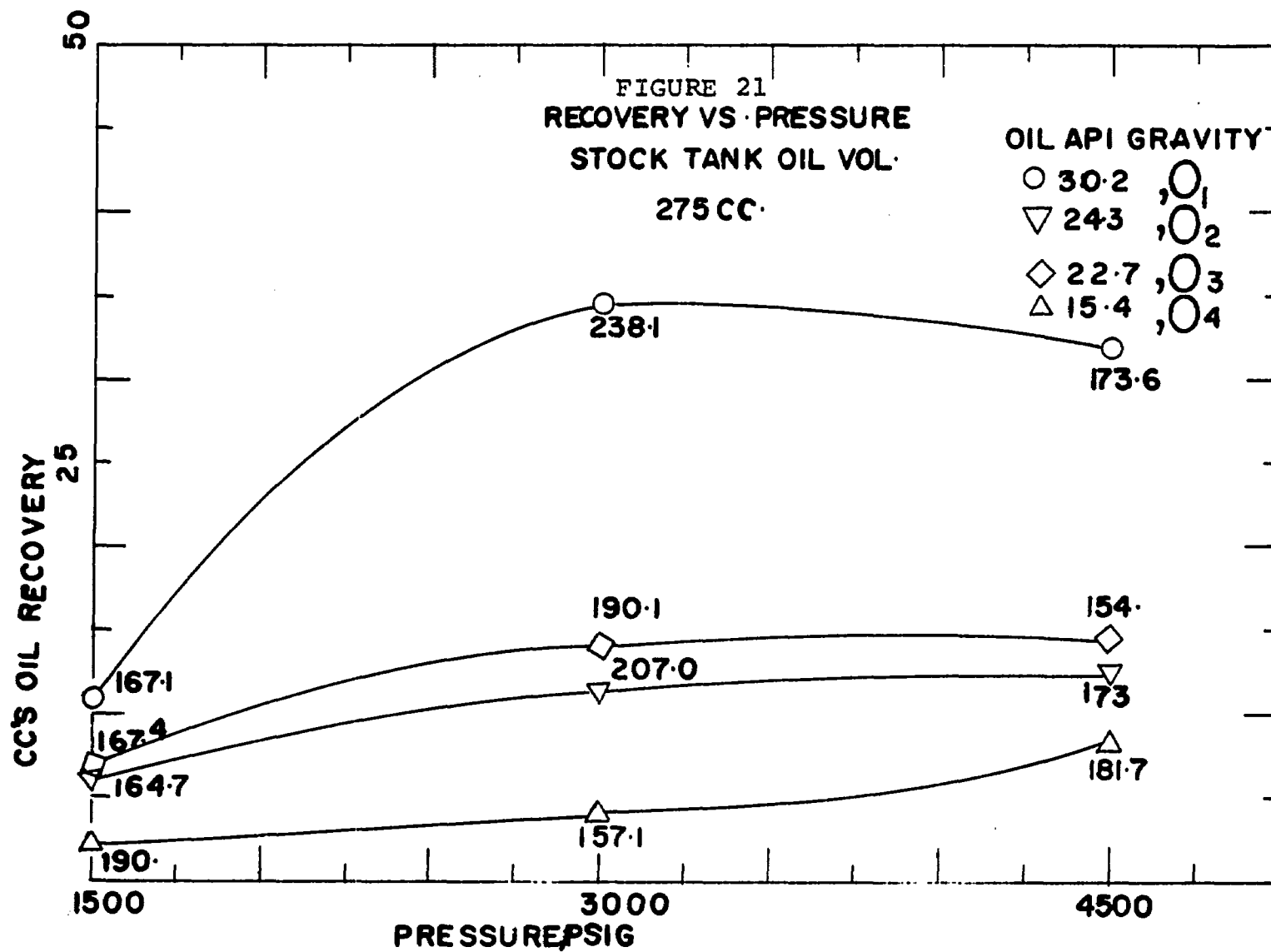
Oil No. 4 (15.4 °API), Pressure A (4500 psig)

Oil gravity, °API	15.4
Equilibrium pressure, psig	4500
Equilibrium temperature, °F	100
Volume of the visual cell, cc Hg at STC	667.047
Volume of the oil sample at STC, cc	275
Volume of mercury withdrawn from the cell equivalent to the oil injected, cc	286.821
Volume of liquid CO ₂ charged into the visual cell at 1500 psig, 34°F, cc	217.584
Volume of mercury withdrawn from the visual cell equivalent to CO ₂ volume charged, cc	277.465
Volume of mercury required to pressurize the oil and mercury in the cell from 14.7 to 4500 psig, cc	52.828
Volume of the gas cap at equilibrium pressure and 100°F, cc	181.675
Volume of the gas produced, measured at STC, cuft	1.6963
Time duration required for condensation, sec	15,200
Volume of the condensate recovered at equilibrium pressure and 100°F measured at STC, cc	8.4
Volume of residual oil recovered, cc	263
B _o , Res. BBL/STB	1.237
Date of the experiment	9-10-71
Volume of the condensate corrected to a gas cap of 167.1 cc, Hg recovered at the same experiment conditions, cc	7.51



results for oils No. 1, No. 2, No. 3 and No. 4, respectively. The plotted data were obtained from Tables 6 through 17. The solid lines in these figures represent the actual recovery of condensate obtained by injection of a certain volume of carbon dioxide which it was hoped would be the volume of carbon dioxide that would produce the same volume of the gas cap in all the runs. This was not always achieved, but was very close to that volume of carbon dioxide needed to produce the same size gas cap represented by the dotted lines. These dotted lines were calculated based on data obtained from the experiments and the same conditions at each point of equilibrium pressure. The numbers indicated on these solid lines represent the actual size of the gas cap obtained.

It is clear from Figures 18 through 21 that the recovery increased as the equilibrium (injection) pressure increased. At a constant temperature, the oil recovery is a function of pressure. It might not be obvious from these figures that the volume of carbon dioxide is sometimes greater than it should be to produce the same size of gas cap at each equilibrium pressure. This results in either a downward concave curve as in Figures 17, 18 and 19, or upward concave curve as in Figure 20. This obscures the better relation of recovery versus pressure which might be a straight line relationship. However, the increase in the recovery at constant temperature as the pressure increase is very clear from the dotted lines since the constant gas cap size at all the



equilibrium pressures was calculated for each of them. A larger size gas cap will produce more oil than a smaller gas cap but this effect was eliminated from the dotted lines. In general they were included in the solid lines. Oil recovery is always increasing from pressure 1500 psig to 3000 psig and from 3000 psig to 4500 psig. This is indicated clearly by the dotted lines; even the solid lines indicate that also. Therefore, the oil recovered is a direct function of the injection (equilibrium) pressure. Figure 17 shows that the oil recovered as indicated by the dotted line at pressure of 1500 psig was 11 cc and it was more than doubled at 3000 psig and almost tripled at 4500 psig. The same behavior is observed in Figures 18 and 19, and almost the same behavior is seen in Figure 20. This phenomenon might be more easily observed from Table 18, Column 6, where the same gas cap size calculation was performed. Prediction above a 4500 psig pressure is not easy and one cannot predict what would happen. If the pressure were increased to 6000 psig, whether it would make oil recovery four times as much as at 1500 psig is unknown. It might be that a completely different relationship exists. Figure 17 implicitly indicates the effect of the size of gas cap injected since at 3000 psig more oil was recovered than at 4500 psig. This was due to the injection of a larger gas cap.

It might be of interest to mention that the increase in the oil recovery by increasing the pressure from 1500 psig

TABLE 18

CONSTANT GAS CAP CALCULATION

Oil Gravity	Equilibrium Pres.	Volume of Gas Cap Recovered at Equilibrium Pressure	Volume of Gas Cap Recovered at STC	Volume of the Condensate Recovered at STC	Volume of Condensate Corrected to Same Gas Cap	B _o Res. BBL STB	Time Required for Orig. Gas Cap to be Liberated sec
°API	psig	psig	cuft	cc	cc		
30.2	1500	167.100	0.7213	11.00	11.00	1.250	8,078
30.2	3000	238.083	1.7813	34.50	24.20	1.303	9,500
30.2	4500	173.643	2.0587	32.00	30.82	1.345	17,910
24.3	1500	164.381	2.2628	5.70	5.80	1.212	14,015
24.3	3000	190.790	3.2124	11.20	9.05	1.230	16,150
24.3	4500	154.037	1.9015	12.50	12.06	1.268	13,643
22.7	1500	167.381	0.7452	6.80	6.80	1.218	19,600
22.7	3000	190.790	1.8610	13.70	12.01	1.257	33,358
22.7	4500	154.037	1.3485	14.50	15.72	1.271	10,931
15.4	1500	190.000	2.4055	2.10	1.85	1.170	10,190
15.4	3000	157.100	1.9983	4.00	4.25	1.226	16,770
15.4	4500	181.675	1.6963	8.40	7.51	1.237	15,200

to 3000 psig is somewhat higher than that increase in oil recovery obtained by increasing the pressure from 3000 to 4500 psig. This is the case in almost all the experiments. In other words the slopes of the lines of the recovery versus pressure in Figure 17 through Figure 20 are greater between 1500 and 3000 psig than the slopes of the corresponding lines between 3000 and 4500 psig. Figure 21 is a superimposition of Figures 17, 18, 19 and 20, and indicates that oil of higher API gravity produces higher recovery. The oil No. 1 recovery line was of the highest value, and consequently was drawn on the top of the figure. Oil No. 4 was of lowest oil recovery values and consequently was drawn on the bottom of the figure. However oil No. 3 of API gravity 22.7 is of higher recovery values than oil No. 2 and was drawn above the recovery line of oil No. 2, which has API gravity of 24.3. This behavior was attributed to better oil composition. It is also indicated by Figure 22. The oil composition will affect the recovery. This fact was established and will be discussed later. The compositions of all the oils were obtained by using a chromatograph and a mass spectrometer. The results indicate that oil No. 3 has more light ends and has a better composition than oil No. 2. The results of these analyses are indicated in Tables 19, 20, 21 and 22.

The formation volume factor at each equilibrium pressure for each oil for each run was calculated in a manner presented in Appendix C. The results of these calculations

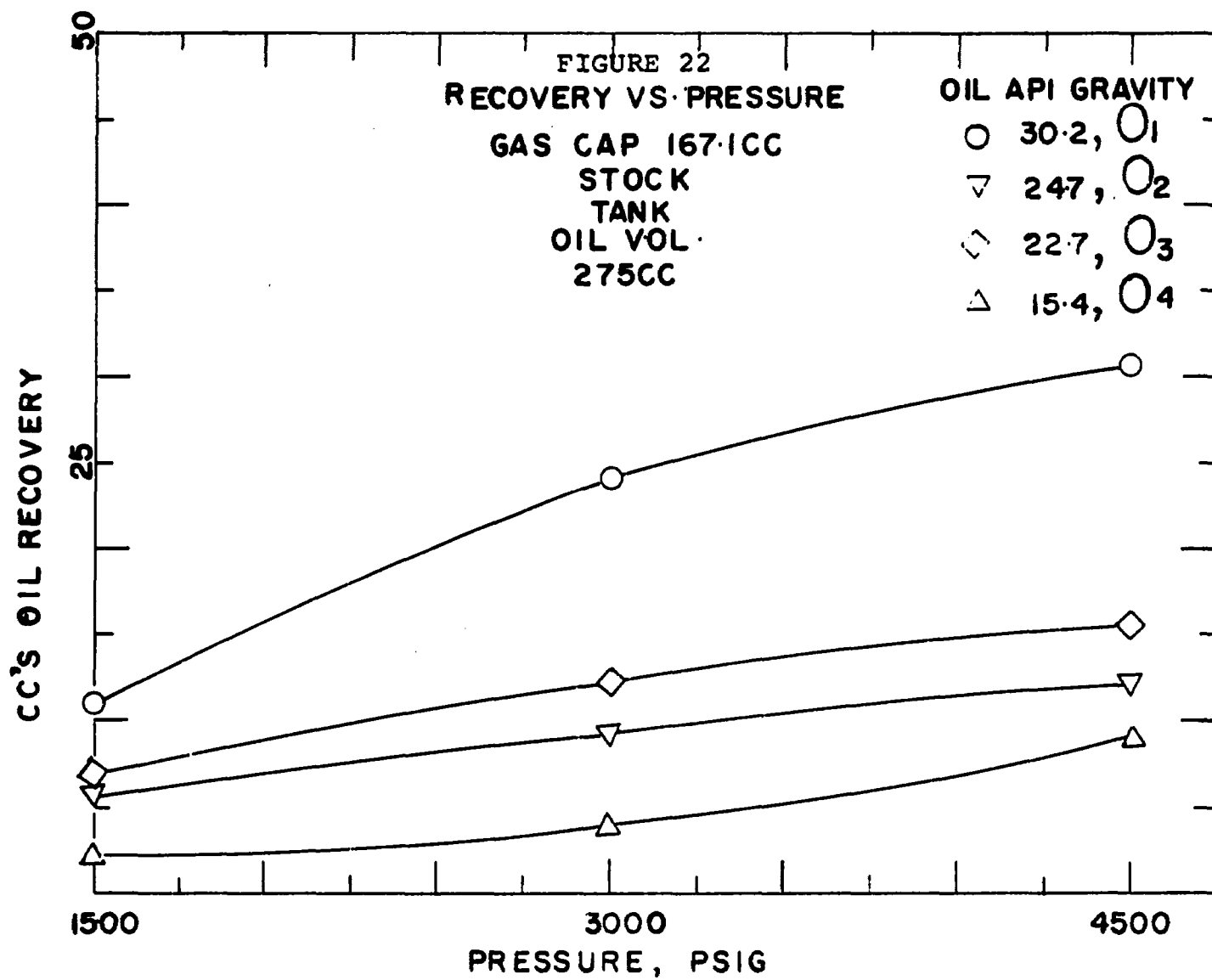


TABLE 19

COMPOSITION BY VOLUME OF OIL NO. 1, 30.2 °API GRAVITY
OBTAINED BY CHROMATOGRAPH AND MASS SPECTROMETER

Component	Content by Volume Percent
C_4H_{10}	2.11
C_5H_{12}	2.46
C_6H_{14}	3.977
C_7H_{16}	8.647
C_8H_{18}	7.298
C_9H_{20}	2.801
$C_{10}H_{22}$	9.131
$C_{11}H_{24}$	32.48
$C_{12}H_{26}$	13.46
$C_{13}H_{28}$	8.78
$C_{14}H_{30}$	8.855

TABLE 20
COMPOSITION BY VOLUME OF OIL NO. 2, 24.3 °API GRAVITY
OBTAINED BY CHROMATOGRAPH AND MASS SPECTROMETER

Component	Content by Volume Percent
$C_{10}H_{22}$	37.364
$C_{11}H_{24}$	16.168
$C_{12}H_{26}$	24.456
$C_{13}H_{28}$	3.804
$C_{14}H_{20}$	2.038
$C_{15}H_{32}$	3.125
$C_{16}H_{34}$	13.043

TABLE 21

COMPOSITION BY VOLUME OF OIL NO. 3, 22.7 °API GRAVITY
OBTAINED BY CHROMATOGRAPH AND MASS SPECTROMETER

Component	Content by Volume Percent
C_4H_{10}	1.474
C_5H_{12}	2.129
C_6H_{14}	4.586
C_7H_{16}	4.750
C_8H_{18}	11.30
C_9H_{20}	7.207
$C_{10}H_{22}$	29.238
$C_{11}H_{24}$	6.224
$C_{12}H_{26}$	1.638
$C_{13}H_{28}$	10.155
$C_{14}H_{30}$	10.155
$C_{15}H_{32}$	2.62
$C_{16}H_{34}$	8.517

TABLE 22
COMPOSITION BY VOLUME OF OIL NO. 4, 15.4 °API GRAVITY
OBTAINED BY CHROMATOGRAPH AND MASS SPECTROMETER

Component	Content by Volume Percent
$C_{12}H_{26}$	10.579
$C_{13}H_{28}$	29.903
$C_{14}H_{30}$	8.502
$C_{15}H_{32}$	13.913
$C_{16}H_{34}$	21.64
$C_{17}H_{36}$	15.458

are presented in Table 18 and in Figure 23. This figure represents formation volume factors versus equilibrium pressure for oils Nos. 1, 2, 3 and 4 used in these experiments.

Figure 23 indicates that the formation volume factor of any oil will increase as the equilibrium pressure increases. That is, the formation volume factor at 4500 psig is of higher value than the formation volume factor at 3000 or at 1500 psig for the same oil at the same experimental conditions. This was clearly indicated by all the oils in the same figure. However, in general, the pressure has less effect on the formation volume factors of oil No. 2 and oil No. 4 than on oil No. 1 and oil No. 3. The lighter the oil used in these experiments, the higher the values of the formation volume factor obtained after carbon dioxide injection. Oil No. 1 was of the lightest gravity and of the best composition in the sense of having more light ends. Therefore its plot of formation volume factor versus pressure is on the top of all the other oils. Oil No. 3 was heavier in gravity than oil No. 2 but of a better composition in having more light ends than oil No. 2. This fact resulted in formation volume factors for oil No. 3 of higher values than the formation volume factors of oil No. 2 as shown in Figure 24. Oil No. 4 was the heaviest in gravity, and it had the least amount of light ends in its composition. Its formation volume factors obtained after carbon dioxide injection were of the lowest values. Its plot is presented in Figure 23 and is the bottom line of all the oils, as was expected.

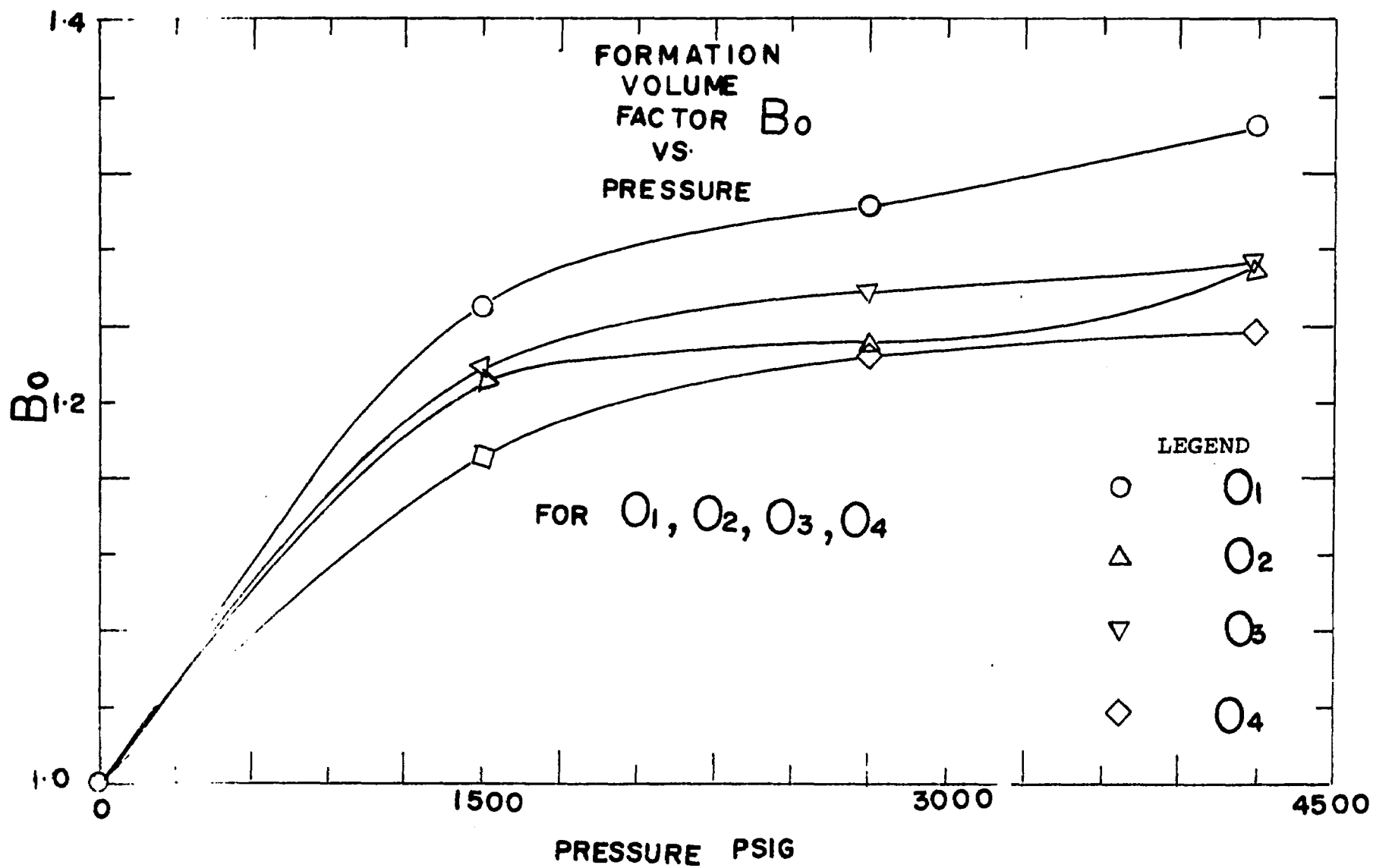
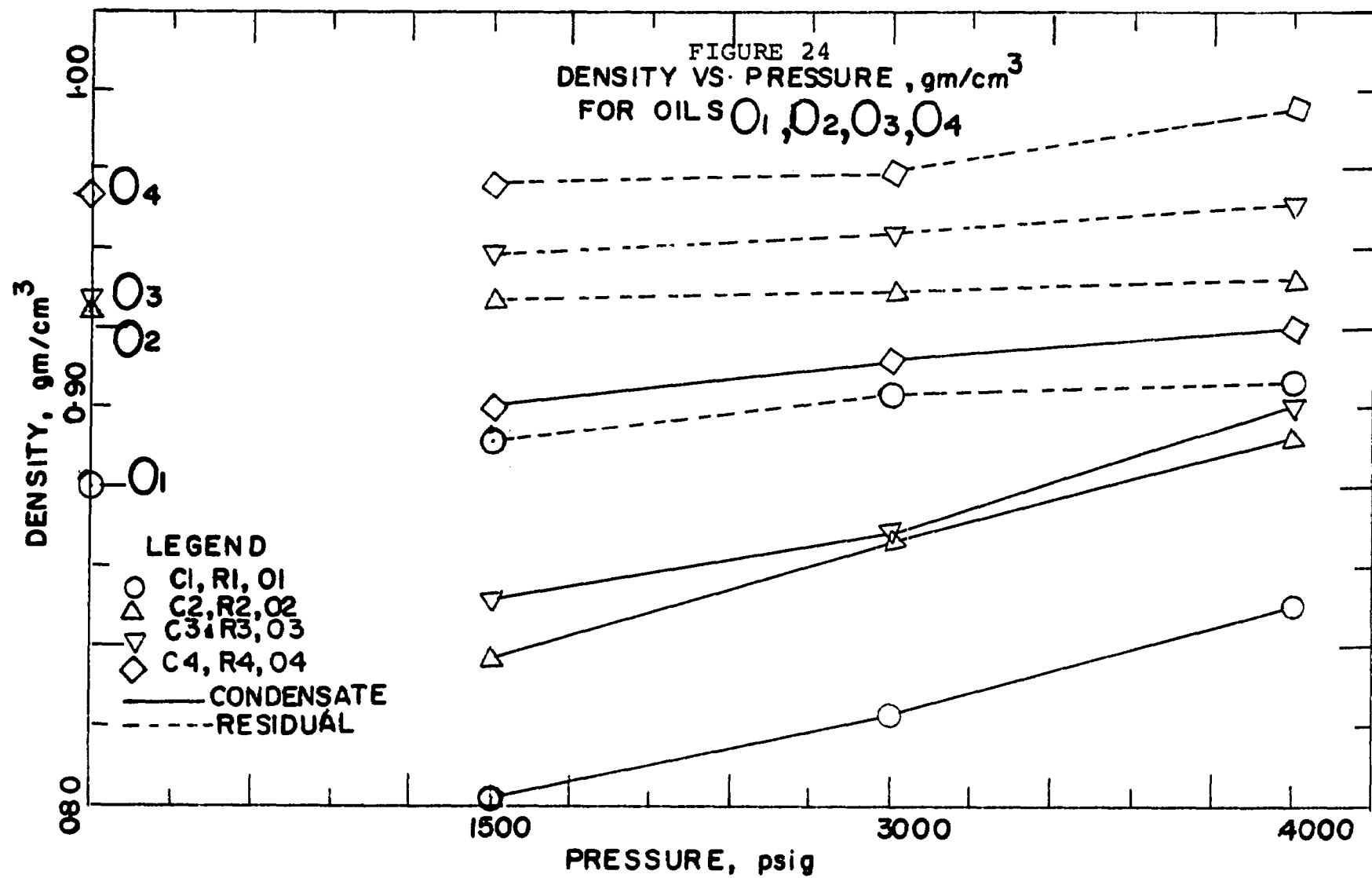


FIGURE 23

From the previous discussion it is clear that the formation volume factors of these oils obtained after carbon dioxide injection must be plotted in a manner similar to the oil recovery versus pressure plots which were shown in Figure 21. A conclusion might be drawn that at constant temperature in these experiments, the formation volume factors of these oils obtained after carbon dioxide injection are functions of pressure, gravity, and composition. The lighter the oil, the more possible it is to increase its formation volume factor by increasing the injection pressure of carbon dioxide.

The densities of these oil samples, condensates and residuals were measured by an analytical balance. The accuracy depends on the quantity of the sample which was available. If there was enough sample, a pycnometer of 25 cc was tried. If there was not enough sample available, other sizes, 10, 5 and 2 cc, were tried. Several times a hydrometer was used if there was a large enough quantity of the sample. All these density measurements were obtained at a temperature of 74°F and at atmospheric pressure. The results of these density measurements are presented in Table 23 and they are plotted in Figure 24. The solid lines of this figure represent the densities of condensates obtained from these experiments after carbon dioxide injection versus the equilibrium pressures of 1500, 3000 and 4500 psig. The dotted lines represent the densities of the residual oils obtained after they were stripped of their condensates versus the same equilibrium pressures.



It is clear from Table 23 and Figure 24 that the densities of the original oil samples, O_1 , O_2 , O_3 and O_4 are greater than the densities of their condensates C_1 , C_2 , C_3 and C_4 (oil recovered) after carbon dioxide injection at 1500, 3000 and 4500 psig. The original oil densities were less than the densities of their residual oils R_1 , R_2 , R_3 and R_4 obtained after recovering the condensates at the indicated equilibrium pressures. Figure 24 indicates that the densities of the condensates and their residuals obtained after condensations always increased as the pressure increased. In other words, the condensate or residual density of any oil is higher at a higher pressure. These lines shown are not perfectly straight lines but they are straight lines between any two equilibrium pressures. They have a positive slope in the direction of increasing the pressure. This figure also indicates that the condensates obtained from oil No. 1 had the lowest density values. They are plotted at the bottom of the graph. Its residuals also showed that their densities were of lower values than all other oil residual densities. However, this means that the densities of the condensates and the residuals of all of these oils were as expected, and they are plotted in the expected sequence. In other words, oil No. 1 has the lowest condensate densities followed by oil No. 2, oil No. 3, and oil No. 4.

The effect of carbon dioxide injection on these oils is clear. It will produce a condensate of lower density than

TABLE 23
DENSITY OF THE HYDROCARBON SAMPLES AT 74°F AND AT
ATMOSPHERIC PRESSURE, GM/CC

Oil Samples	Condensates	Residuals
$O_1 = 0.8794$	C_1A 0.8500	R_1A 0.9065
	C_1B 0.8230	R_1B 0.9036
	C_1C 0.8020	R_1C 0.8916
$O_2 = 0.9230$	C_2A 0.8920	R_2A 0.9322
	C_2B 0.8660	R_2B 0.9291
	C_2C 0.8370	R_2C 0.9279
$O_3 = 0.9260$	C_3A 0.9000	R_3A 0.9516
	C_3B 0.8980	R_3B 0.9440
	C_3C 0.8520	R_3C 0.9390
$O_4 = 0.9535$	C_4A 0.9200	R_4A 0.9759
	C_4B 0.9120	R_4B 0.9593
	C_4C 0.9000	R_4C 0.9567

MOLECULAR WEIGHT
VS. PRESSURE
FOR OILS, O_1, O_2, O_3, O_4

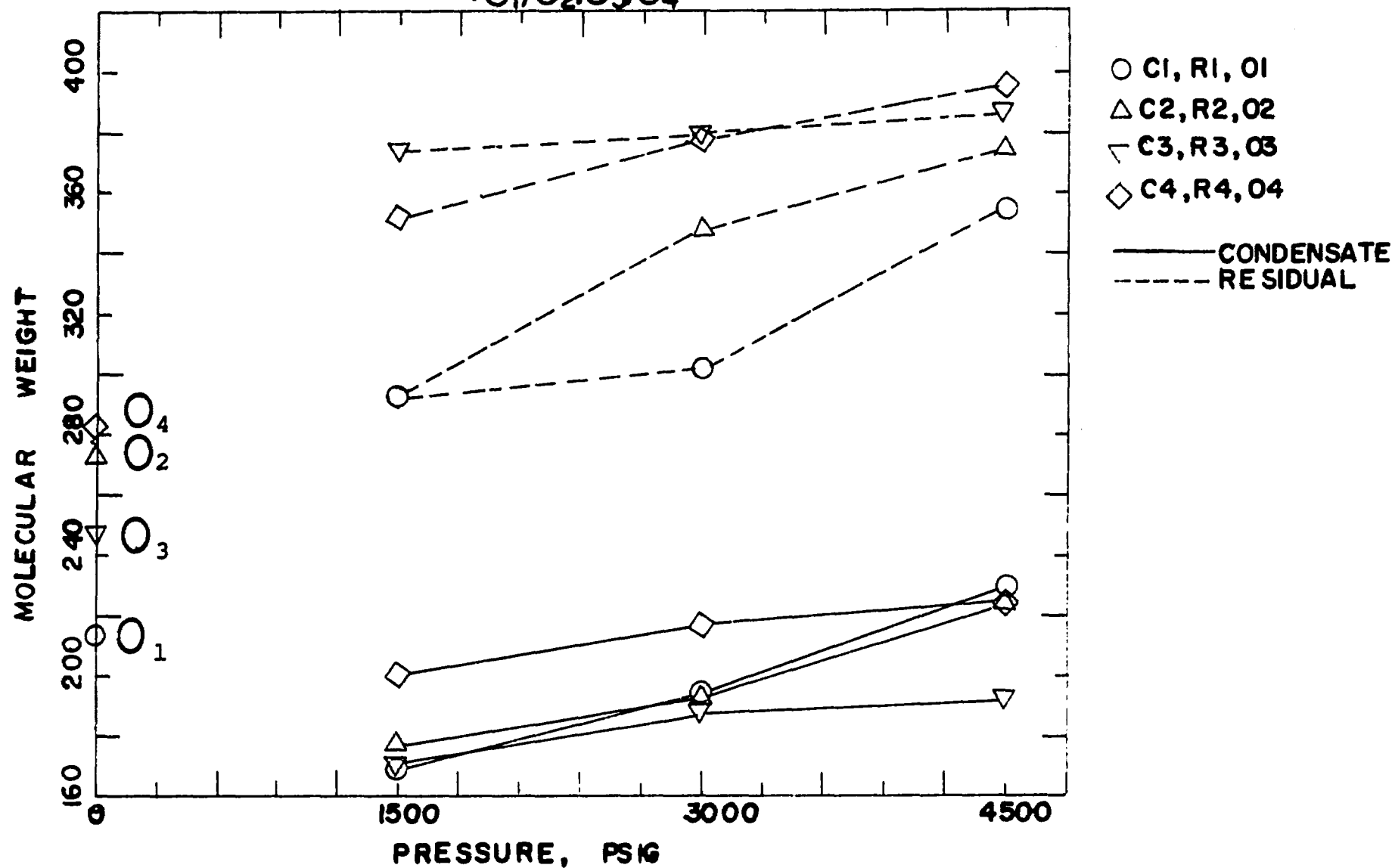


FIGURE 25

the original oil and a residual oil of higher density than the original oil. The slopes of the condensate lines of oil No. 1, oil No. 2 and oil No. 3 are higher than the slopes of the condensate lines of oil No. 4. However, the condensate lines in general have a higher slope than their residual lines. Even oil No. 1 has responded to a change in the density of its condensate and of its residual line much more than oil No. 4.

The molecular weights of the original oil samples and their condensates obtained after the carbon dioxide injection and their residuals were measured by a standard freezing point depression method. The results of these measurements are presented in Table 24 and they are plotted in Figure 25 as molecular weight versus equilibrium pressures. The dotted lines in this figure represent the molecular weights versus pressures of the residual oil, while the solid lines represent the molecular weights versus pressures of the condensates. It is clear from this figure that the condensates' molecular weights are always lower than the molecular weight of the original oil samples and much lower than the molecular weight of their residuals. This fact was clearly indicated by oils No. 1, No. 2, No. 3 and No. 4. The molecular weights of the condensates and their residual oils always increased as the pressure increased. For instance in Figure 25 the molecular weight of the condensate at 1500 psig is less than the molecular weight of the condensate of the same oil obtained after injection of carbon dioxide at 3000 psig and much lower

TABLE 24
EXPERIMENTAL MOLECULAR WEIGHT DATA AND RESULTS

Samples	Weight of Solvent gms	Weight of Solute gms	Freezing Point of the Solution °F	Weight of Solute per 1000 gms of Solvent gms	Freezing Point Depres- sion Δt_f °F	Molality Moles of Solute per 1000 gms of Solvent	Molecular Weight of Solute
C ₁ A	13.2175	0.3568	3.72	27.80	0.62	0.1211	229.0
C ₁ B	12.2457	0.3646	3.56	29.80	0.78	0.1523	195.3
C ₁ C	12.7473	0.5570	3.02	43.70	1.32	0.2580	169.2
C ₂ A	13.5503	0.6405	3.26	47.20	1.08	0.2110	223.0
C ₂ B	13.6200	0.5802	3.21	42.60	1.13	0.2205	193.1
C ₂ C	13.5132	0.6920	3.86	51.20	1.48	0.2890	177.3
C ₃ A	12.8003	0.5483	3.21	42.60	1.13	0.2210	192.5
C ₃ B	13.4233	0.5858	3.16	43.60	1.18	0.2310	188.4
C ₃ C	12.9824	0.6035	2.95	46.50	1.39	0.2710	171.7
C ₄ A	12.7484	0.5957	3.27	46.70	1.07	0.2090	223.5
C ₄ B	13.5227	0.4238	3.60	31.30	0.74	0.1445	217.0
C ₄ C	13.0234	0.2744	3.80	21.05	0.54	0.1050	200.0
R ₁ A	13.2947	0.4685	3.83	35.30	0.51	0.0996	355.0
R ₁ B	13.0898	0.4967	3.70	37.95	0.64	0.1250	303.0
R ₁ C	12.3293	0.5252	3.60	42.60	0.74	0.1445	292.0

TABLE 24--Continued

Samples	Weight of Solvent gms	Weight of Solute gms	Freezing Point of the Solution °F	Weight of Solute per 1000 gms of Solvent gms	Freezing Point Depres- sion Δt_f °F	Molality Moles of Solute per 1000 gms of Solvent	Molecular Weight of Solute
R ₂ A	12.6362	0.5430	3.75	43.00	0.59	0.1152	375.0
R ₂ B	12.4074	0.6006	3.63	48.00	0.71	0.1386	348.5
R ₂ C	12.8792	0.5120	3.64	40.00	0.70	0.1365	293.0
R ₃ A	13.5134	0.4834	3.87	35.7	0.47	0.0918	387.0
R ₃ B	12.8123	0.5804	3.73	45.2	0.61	0.1190	380.0
R ₃ C	13.5329	0.7674	3.56	56.2	0.78	0.1502	374.5
R ₄ A	13.1224	0.5500	3.81	41.80	0.53	0.1035	396.0
R ₄ B	13.0406	0.4089	3.92	31.03	0.42	0.0820	378.0
R ₄ C	11.9703	0.3710	3.89	31.00	0.45	0.0880	352.0
O ₁	12.5427	0.4813	3.50	38.30	0.84	0.1640	233.0
O ₂	13.2413	0.7013	3.35	52.90	0.99	0.1932	273.0
O ₃	12.2926	0.2376	3.94	19.34	0.40	0.0782	247.5
O ₄	12.6097	0.2847	3.93	22.60	0.41	0.0808	282.0

than the molecular weight of its condensate obtained at 4500 psig. This was clearly indicated by all the oils. The molecular weight of oil No. 1 was lower than for all the other oils. This is seen from Figure 25. This might be expected since oil No. 1 was of lower density than all the other oils. This phenomenon was not true with oil No. 3 since it was heavier than oil No. 2, but had a molecular weight lower than oil No. 2. Even the molecular weights of the condensates obtained from oil No. 3 were much lower than the molecular weights of the condensates obtained from oil No. 2. In general the slopes of the condensates and the residual oils obtained from oils No. 1, No. 2 and No. 3 are higher than the slopes of the condensates and the residuals of oil No. 4. This means that carbon dioxide injection has reduced the molecular weight of the other three oils more than for oil No. 4

Table 25 is a material balance calculation to predict the loss of the light ends that were picked up by carbon dioxide in the vapor phase during evaporization and were not condensed during the condensation. These light ends could not be identified by the chromatograph and it is conjectured that the chromatograph was not functioning properly. This table contains some data obtained from Tables 19 through 22 and Tables 6 through 17 from which the data fed into the computer program were obtained. Data in Table 25 were calculated in a manner similar to that in Appendix D. The calculation was performed on the same gas cap size in all the experiments. This was

TABLE 25
MATERIAL BALANCE CALCULATION TO PREDICT THE LOSS, ASSUMING CONSTANT
GAS CAP AND THE SAME VOLUMETRIC LOSS

Oil Grav- ity	Equi- lib. Pres.	Volume of CO ₂ Injected at 1500 psig 34°F into System	CO ₂ Pro- duced at Equi- librium Pressure Measured at STC	Moles of Oil Injec- ted at STC	Volume of CO ₂ Disslvd in Vapor Phase	Volume of CO ₂ Disslvd in Liq. Phase at Equilib. Pressure	Total No. of Moles Fed into System	Moles of the Light Ends Lost	Moles of CO ₂ In- jected into the System at Equi- librium Pres. & Temp.
°API	psig	cc	stcuft		cc	cc		%	
30.2	1500	203.039	0.7213	1.032	36.420	166.619	5.312	0.0354	0.807
30.2	3000	197.000	1.2500	1.032	63.000	133.768	5.195	0.0386	0.802
30.2	4500	216.200	1.9800	1.032	100.000	116.200	5.602	0.0555	0.816
24.3	1500	207.000	2.3050	0.930	116.200	90.800	5.300	0.0123	0.825
24.3	3000	202.050	2.5950	0.930	130.400	71.650	5.200	0.0372	0.820
24.3	4500	214.000	1.8300	0.930	92.800	121.200	5.460	0.0442	0.830
22.7	1500	191.693	0.7452	1.030	46.000	145.693	5.080	0.0662	0.798
22.7	3000	181.300	1.5730	1.030	79.300	102.000	4.860	0.0685	0.788
22.7	4500	217.900	1.4610	1.030	73.700	144.200	5.630	0.0696	0.817
15.4	1500	183.400	2.1100	0.922	106.500	76.400	4.792	0.0387	0.809
15.4	3000	210.000	2.1300	0.922	107.200	102.800	5.362	0.0447	0.827
15.4	4500	201.000	1.5600	0.922	78.500	122.500	5.162	0.0494	0.824

necessary to obtain the amount of the loss. However all the other conditions were maintained to be as those performed in the experiments. Also it was necessary to assume a volumetric loss of about 5 cc. This was almost 1.8 percent of the total oil injected into the system.

The calculation of these factors in these tables indicates that, from ten experiments out of a total number of twelve, the mole fraction of carbon dioxide injected has to be more than 80 mole percent of the feed in order to produce some of the recoverable oil. Even in the other two experiments, the carbon dioxide mole percent in the feed injected was 79.8 and 78.8. Generally the injected carbon dioxide volume has to be more than 80 mole percent of the total feed into the system in order to produce some recoverable oil. This certainly depends on oil composition, oil specific gravity and oil molecular weight, keeping all other factors, such as pressure and temperature, constant. It was noticed that with 80.9 mole percent of the feed being carbon dioxide injected in oil No. 4, the oil recovery was 2 cc out of 275 cc of the original oil samples injected at 1500 psig. This is less than 0.8 percent of the oil in place recovered. This is certainly a reflection of the effect of gravity and the composition of the oil recovery, keeping in mind all the other factors, pressure temperature, size of the gas cap and the oil volume injected are constant.

In the twelve experiments indicated in Table 25, the lost very light ends were picked up by the carbon dioxide during evaporation and they were not condensed during the condensation. These light ends went out through the condenser to the wet-testmeter. They were calculated by a material balance equation in a manner presented in Appendix D, and their results were presented in Table 25. The results indicate in all the experiments that the loss is of higher values at 4500 psig pressure than the loss values obtained at 1500 or at 3000 psig. It might be of interest to mention that the lighter the oil the more the loss occurring at the same experimental conditions. This might be expected since the lighter oil is supposed to have more lighter ends and a greater loss is expected. This was indicated by oil No. 1 and oil No. 3 since they were the lightest oils. Their loss was greater than oil No. 4 and oil No. 2 since they were heavier. It was noticed from those experiments that the amount of carbon dioxide dissolved in the vapor phase of oil No. 1 and oil No. 3 is less than that dissolved in the vapor phase of oil No. 4 and oil No. 2. This was also indicated by Column 6 of Table 25. This phenomenon is believed to be attributed to the fact that oil No. 1 and oil No. 3 have a better composition than oil No. 4 and oil No. 2. The amount of gas dissolved in the vapor phase of oil No. 1 and oil No. 3 was also directly proportional to the equilibrium pressure (see Table 25, Column 6). This happened with a constant number of

moles (1.032) of oil being fed into the system. This phenomenon was somewhat indicated by oil No. 3, but it was not by oil No. 2 or oil No. 4. The latter two oils showed that more carbon dioxide gas was dissolved at a higher pressure of 3000 psig but not at 4500 psig.

The amount of the vapor stripped out of the condensate in the vapor phase at the equilibrium pressure and 100°F was measured by the wet-testmeter. They were obtained at equilibrium pressure as indicated by column 4 of Table 25, and were also proportional to the pressure. There was a greater amount of gas liberated at higher pressure from oil No. 1, and the behavior was almost the same for oil No. 3. But it was not the same for oil No. 4 and oil No. 2. They indicated that more gas was liberated at 3000 psig. It was fortunate that almost the same gas cap size of carbon dioxide was injected in the same number of moles of oil in the system of oil No. 1 and oil No. 3 in experiment No. 1 and No. 7, respectively, at 1500 psig equilibrium pressure (Tables 6 and 12 respectively). This was performed with all other conditions being the same in both cases but still the same amount of gas was not liberated from their vapor phases. In oil No. 3 a greater gas cap was recorded by the wet-testmeter than for the gas liberated from oil No. 1. This indicates also the effect of composition and gravity on the amount of gas that could be dissolved in the liquid phase or liberated from the vapor phase at a certain equilibrium pressure and temperature. The fact is that more

gas was recovered from the vapor (obtained with the condensation) from the heavier oils, oils which have more heavier ends in their composition like oils No. 2 and No. 4. The time duration which was required for condensation was longer at the higher equilibrium pressure. This might be due to the fact that more gas was dissolved at the higher pressure; thus more could be produced. This was indicated by oil No. 1.

It was thought that it might be of interest to recognize some variables obtained from these experiments such as B_o , K_{CO_2} , M , m , S_{wo} , C_o , $CGOR$, R_s , GC , and CGO . Their meanings are indicated in Appendix B, their methods of calculation are explained in Appendix F and their values are presented in Table 26. The K values of CO_2 were calculated in Appendix E and presented in Table 27. All of these variables were presented in plots of their values versus the experimental equilibrium pressure. This was performed to establish the effects of carbon dioxide, injection pressure, gravity and composition on oil recovery. Those factors were obtained and analyzed from the data obtained from the original experiments and indicated by Tables 6 through 17. The behavior of these variables in the figure is clear. The size of the gas cap was always plotted due to its importance in simplifying the prediction of the behavior of those factors due to the carbon dioxide injection effect and the pressure effect on oil recovery. It is not very easy to tell much about the behavior of these variables since there are many variables in the graph. However,

TABLE 26
RESULTS OF CALCULATION OF VARIABLES OBTAINED FROM THE EXPERIMENTS*

Oil Grav- ity	Pres- sure	Compres- sibility CGO	Forma- tion Volume Factor B_o ResBBL STB	Ratio of Res. Size of Gas Cap to Res. Oil Vol. M	GOR SCUFT Per STBL	S_{wo} %	$C_o \times 10^6$ cc/cc psi	GCOR SCUFT Per Res. BBL	m SCUFT Per Res. BBL	R_s SCUFT Per STB	GC cc
API	psig	$\frac{cc}{275cc/P}$									
30.2	1500	5.242	1.250	0.506	10,400	4.25	12.70	2030	1600	728	167.100
30.2	3000	30.400	1.303	0.762	8,230	15.00	15.80	3230	2400	825	238.083
30.2	4500	39.770	1.345	0.531	10,220	11.50	12.20	2340	1680	1090	173.643
24.3	1500	5.883	1.212	0.504	63,200	4.13	14.20	2000	1585	450	164.007
24.3	3000	28.448	1.232	0.638	45,600	2.08	14.01	2510	2100	873	207.007
24.3	4500	37.763	1.268	0.519	24,200	4.50	9.90	2040	1655	925	173.000
22.7	1500	3.278	1.218	0.512	17,450	2.16	7.80	1960	1618	286	167.381
22.7	3000	23.708	1.257	0.580	21,600	1.00	11.50	2410	1900	900	190.790
22.7	4500	38.240	1.271	0.480	14,750	3.31	12.05	1950	1471	970	154.037
15.4	1500	3.700	1.171	0.596	182,000	9.90	8.90	2220	1878	532	190.000
15.4	3000	30.163	1.226	0.473	79,400	2.30	11.70	1900	1495	887	157.100
15.4	4500	52.828	1.237	0.550	32,100	7.90	11.70	2260	1578	1145	181.675

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*Their meanings are presented in Appendix B.

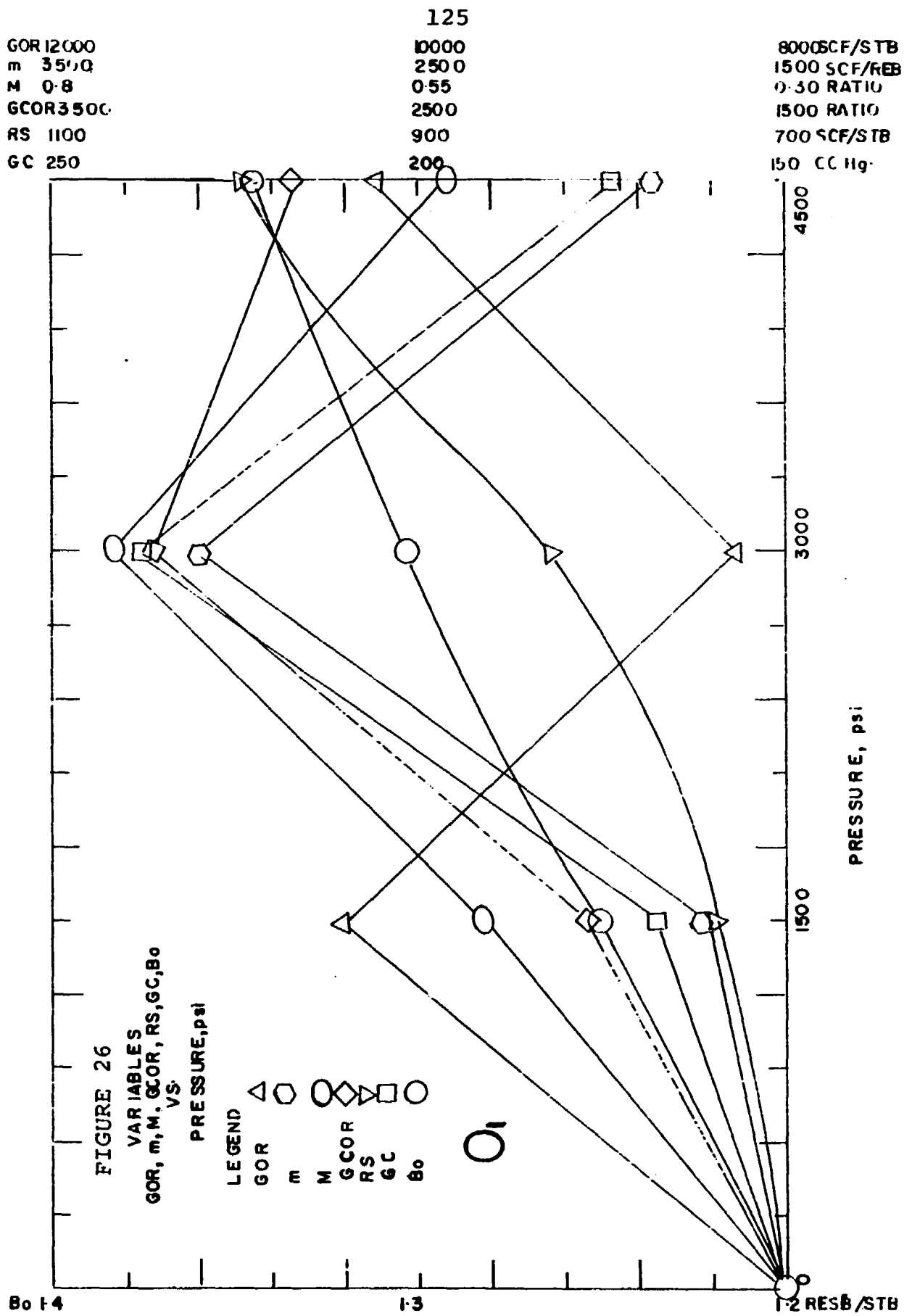
TABLE 27

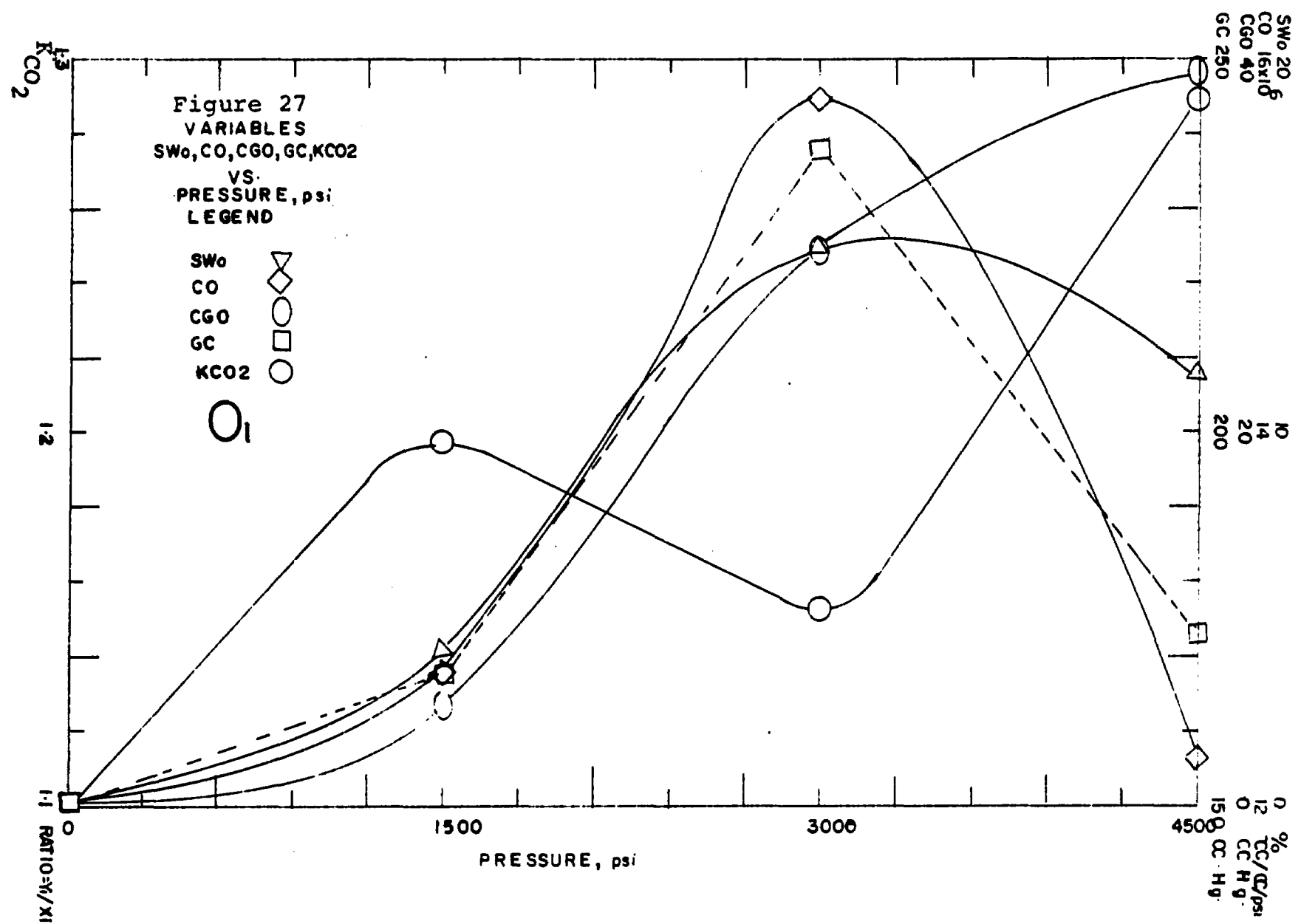
DATA CALCULATED AND FED INTO THE COMPUTER PROGRAM

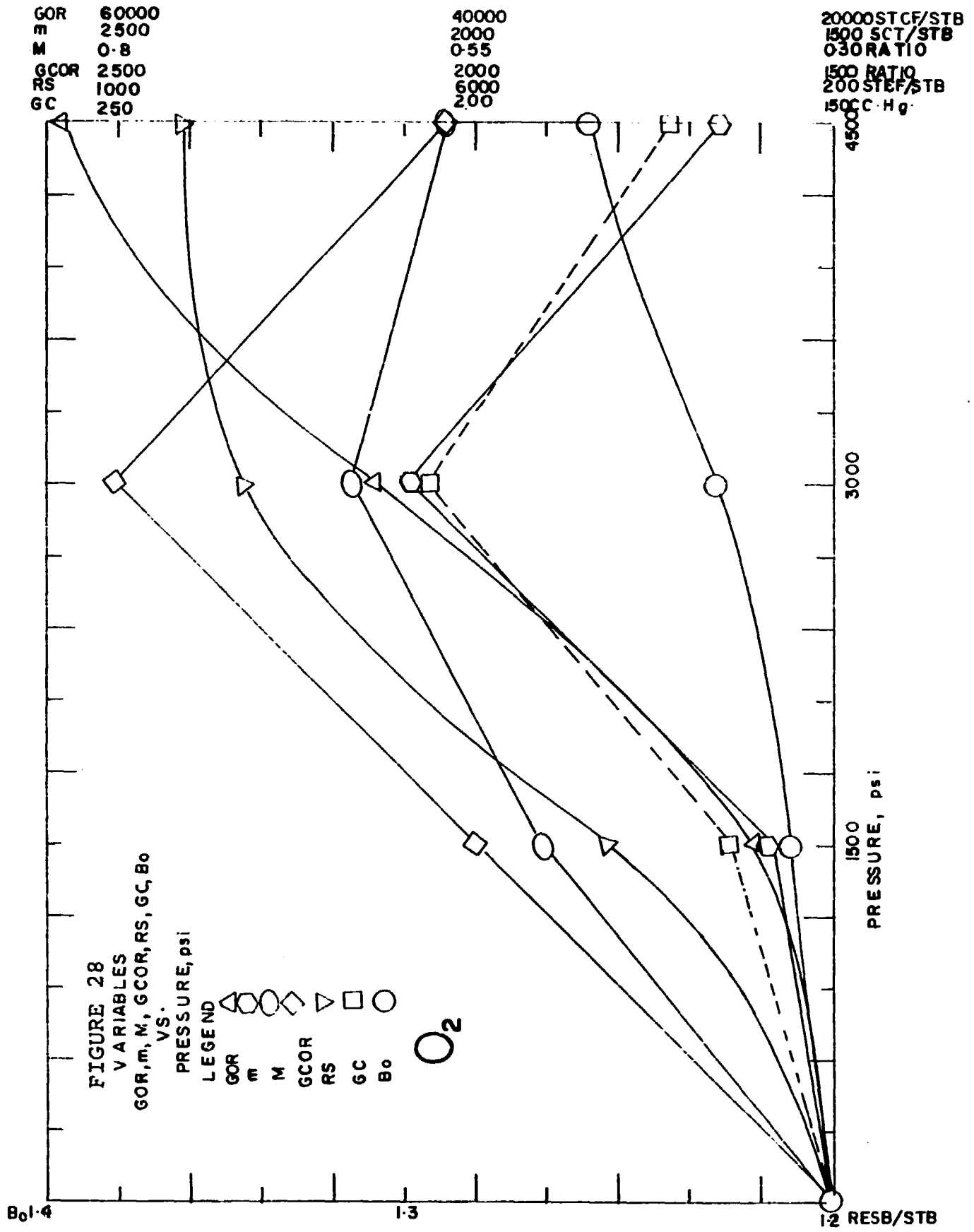
Oil No. 1	Molecular Weight	Critical Temperature °F	Pressure, psig					
			4500		3000		1500	
			Z	K	Z	K	Z	K
CH ₄	16.04	-116.7	0.04	1.55	0.001	1.95	0.03	3.0
C ₂ H ₆	30.060	89.770	0.01	0.85	0.0190	0.8	0.01	0.8
C ₃ H ₈	44.090	205.950	0.0034	0.6	0.005	0.5	0.0054	0.4
C ₄ H ₁₀	58.120	305.130	0.00268	0.4	0.120+	0.326	0.1576+	0.192
C ₅ H ₁₂	72.146	385.60	0.12392	0.32				
CO ₂	44.010	87.90	0.82	1.315	0.855	1.315	0.807	1.75
Recovery, cc (Condensate)			32.253		36.55		11.509	
Oil No. 3								
CH ₄	16.04	-116.7	0.04	1.55	0.039	1.95	0.001	3.00
C ₂ H ₆	30.060	89.770	0.01	1.37	0.001	0.80	0.069	0.80
C ₃ H ₈	44.090	205.950	0.0028	0.6	0.0024	0.50	0.002	0.40
C ₄ H ₁₀	58.120	305.130	0.0021	0.46	0.1476+	0.323	0.13093+	0.193
C ₅ H ₁₂ ⁺	72.146	385.60	0.141+	0.312				
CO ₂	44.010	87.90	0.805	1.37	0.81	1.37	0.797	1.75
Recovery, cc (Condensate)			16.298		15.430		7.676	

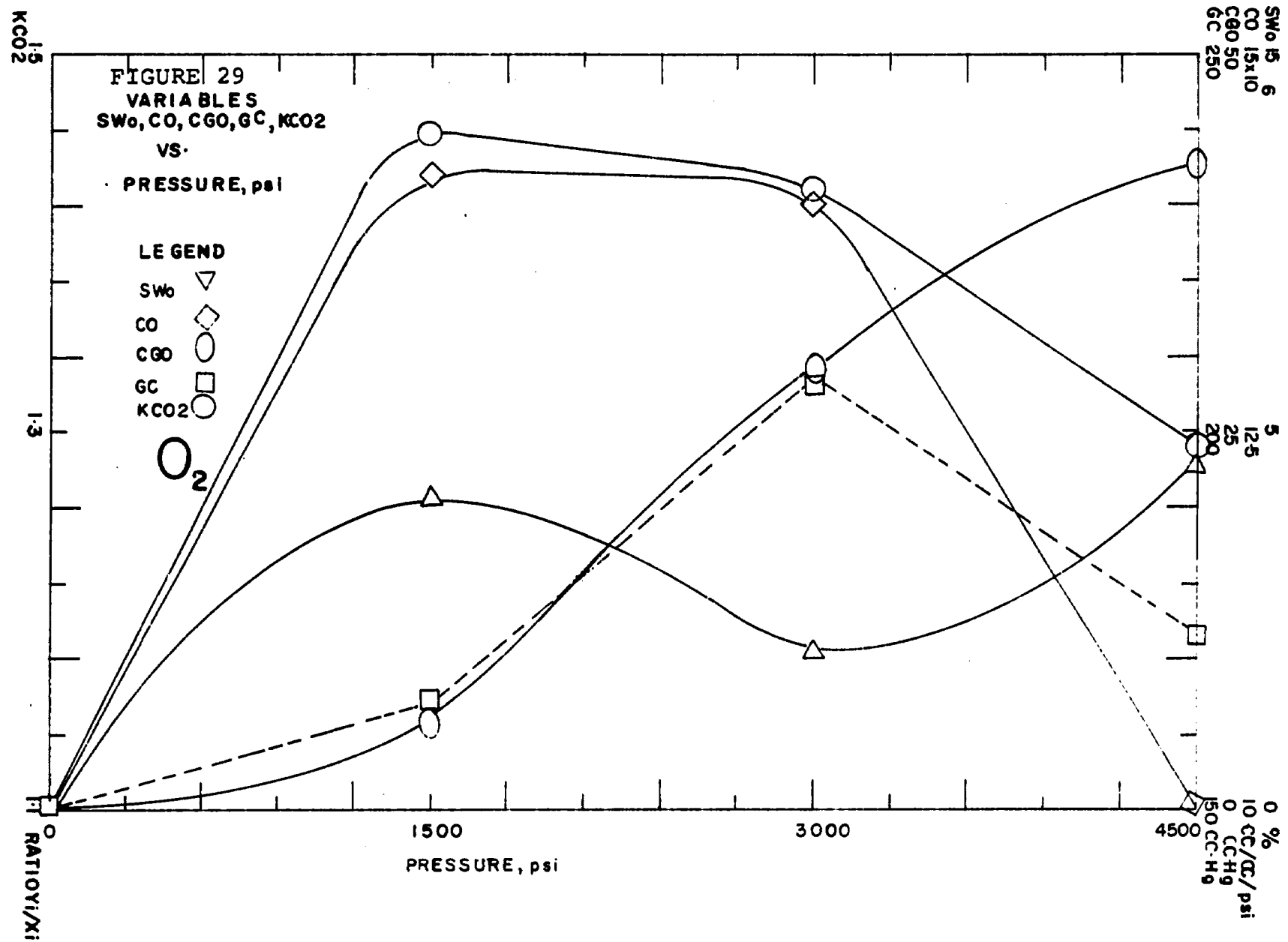
B_o , R_s and CG_o figures show the same trend of the behavior, and they are increasing as the pressure increases. These variables showed higher values at higher pressures, while M , m , $GCOR$, GC and K_{CO_2} followed almost the same trend. But each one of these variables has its own behavior as indicated in Figures 26 through 33. Figures 26 and 27 represent the variable values versus pressure for oil No. 1 and Figures 28 and 29 for oil No. 2, Figures 30 and 31 for oil No. 3, and Figures 32 and 33 for oil No. 4. Figure 34 represents the compressibility or shrinkage of the gas cap and the oil, the expansion of the cell and compression of the mercury at each equilibrium pressure obtained from these experiments plotted versus the equilibrium pressure. This is represented by the solid lines. The dotted lines represent the actual size of the gas cap which was injected in these experiments. It is clear these solid lines are increasing at higher pressure. This might be expected, but this behavior was much higher for oil No. 4 than for oils No. 1, No. 2 and No. 3.

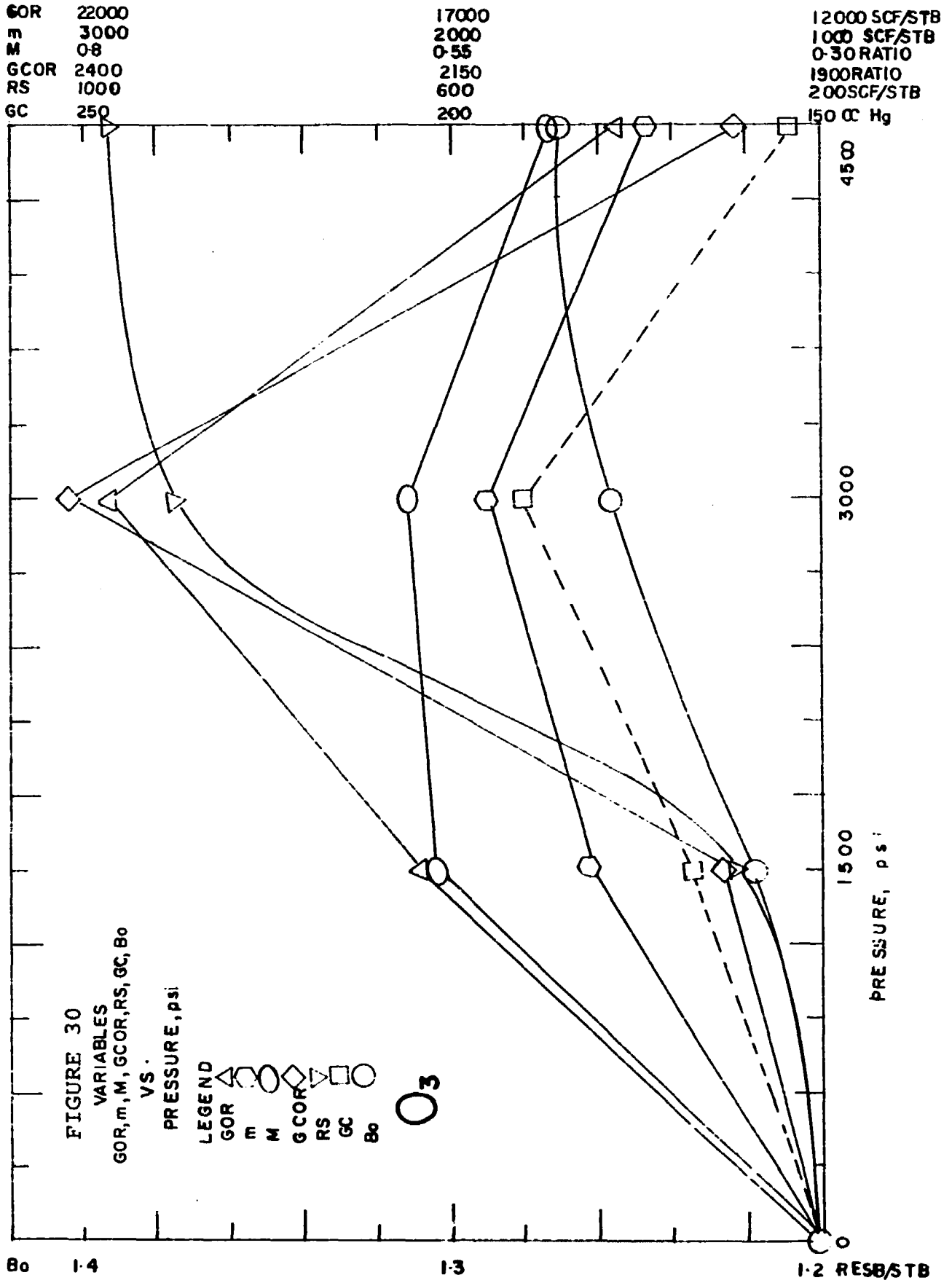
The data fed into the computer program are calculated in Appendix D and presented in Table 27. The K values of carbon dioxide at 4500 and 3000 psig were assumed for a convergence pressure of 10,000 psig. They are calculated in Appendix E and presented in Table 28. The K values of the other components and at other pressures were obtained from Reference 30 with a very minor adjustment to some of them due to the absence of the heavy oil components. The adjustment

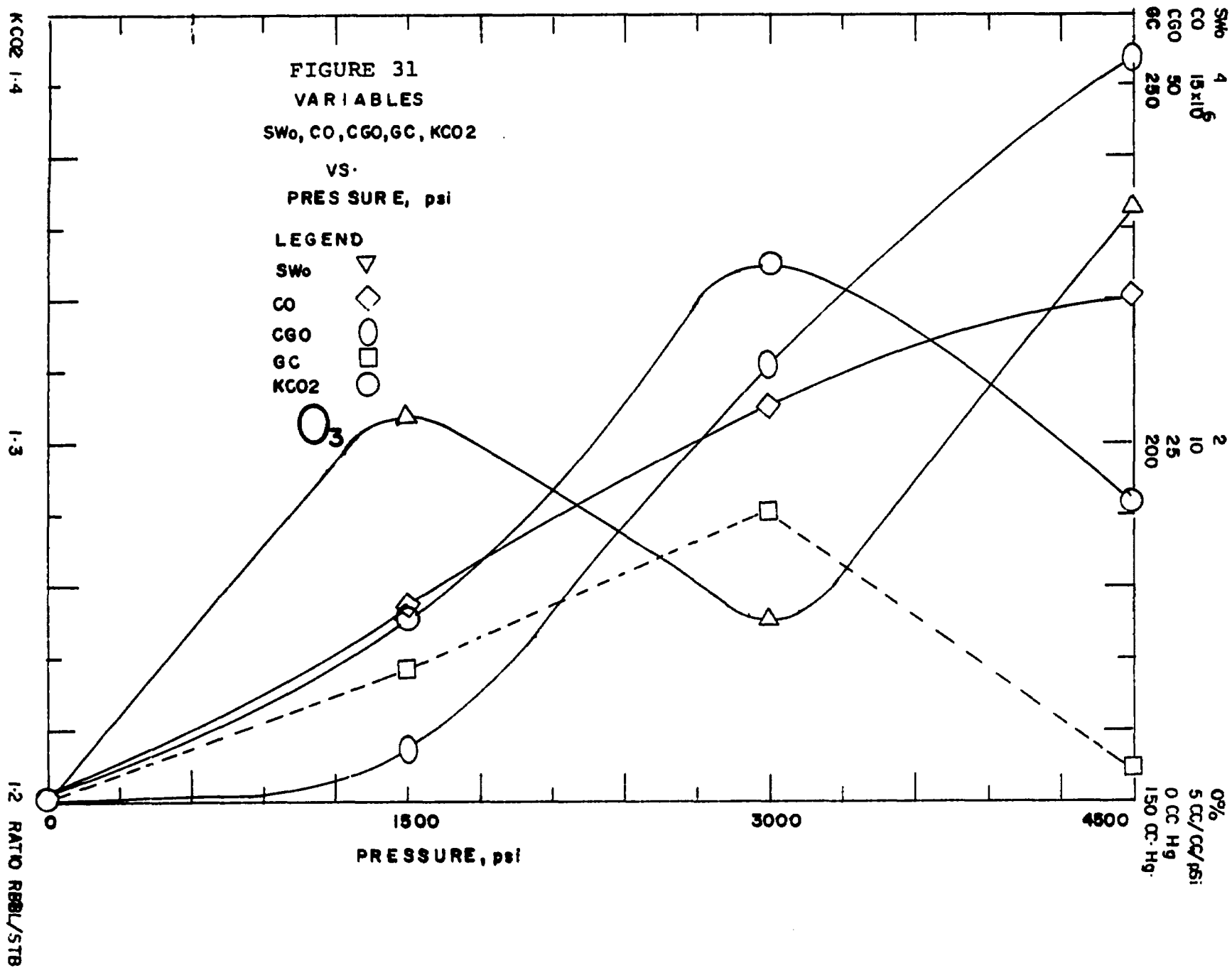


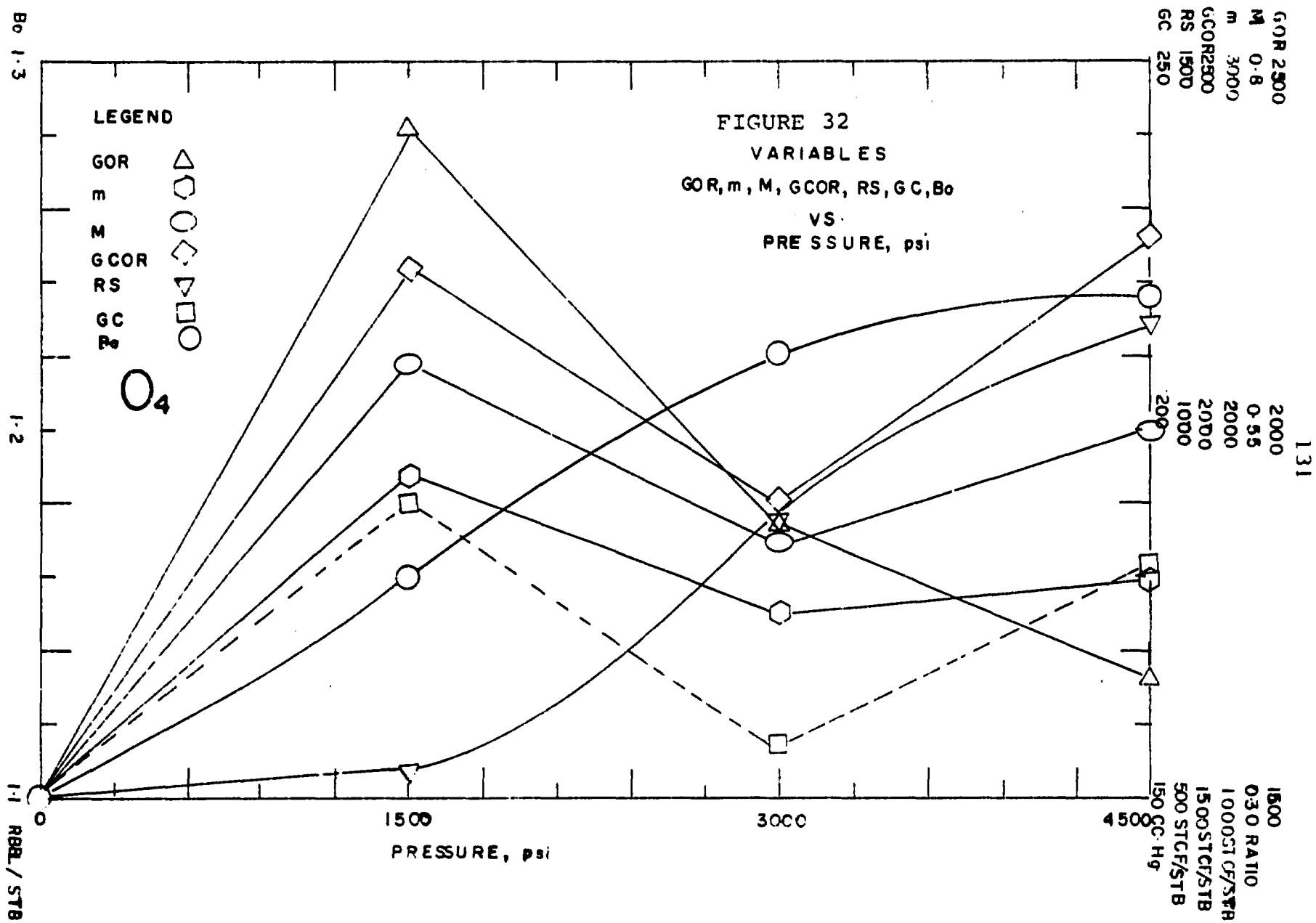


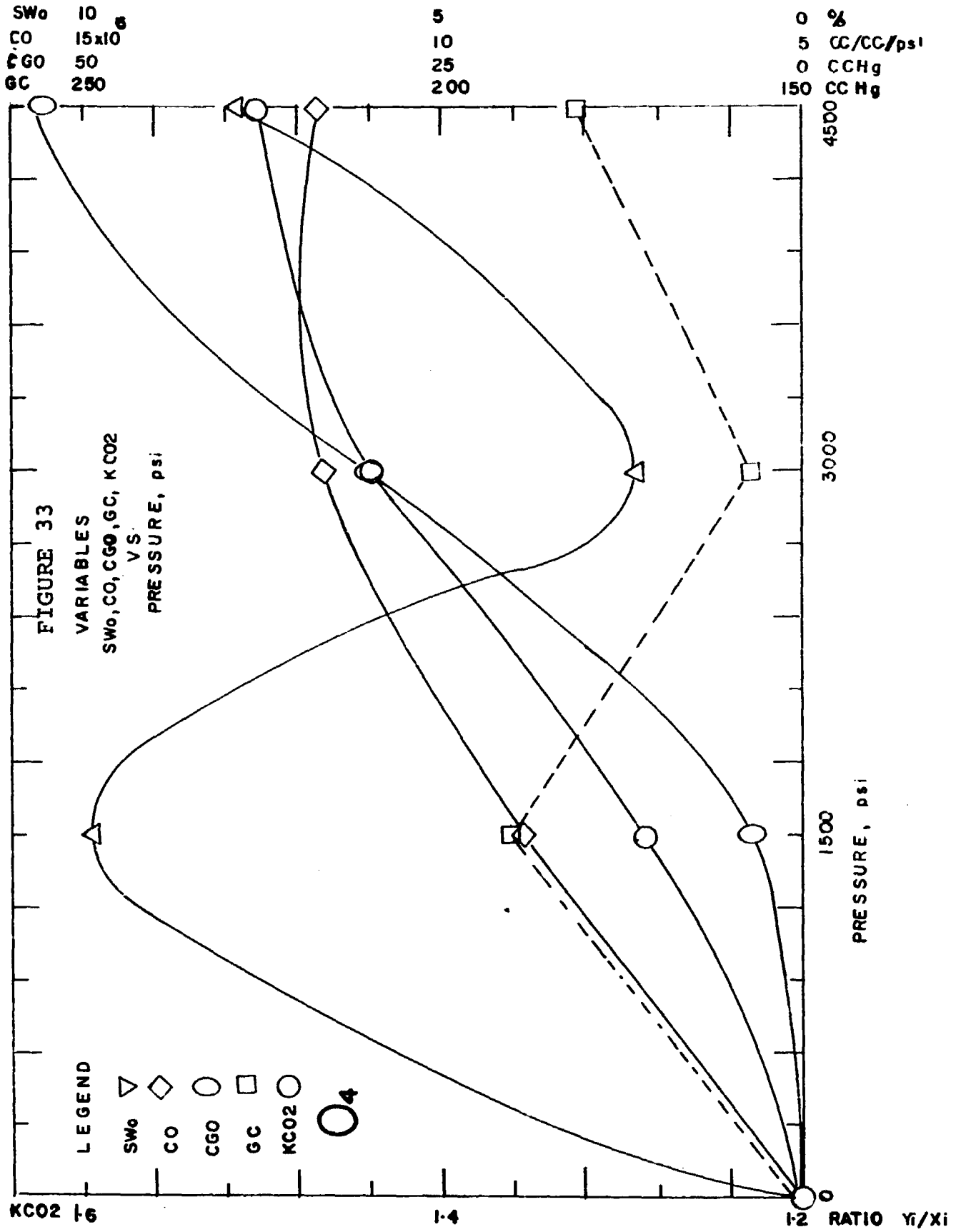












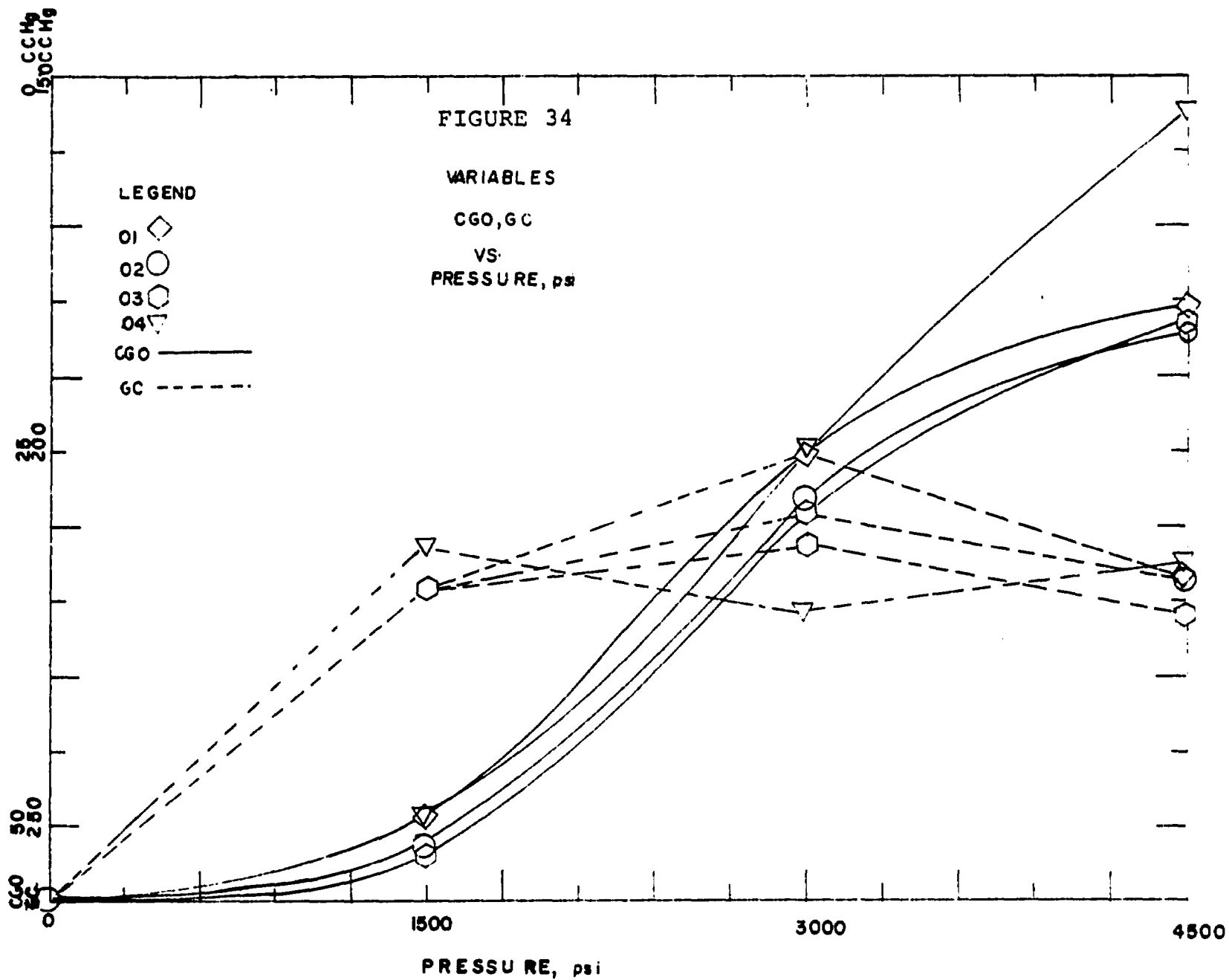


TABLE 28
EXPERIMENTAL RESULTS OF K VALUES OF CARBON DIOXIDE
CALCULATED AT THE EQUILIBRIUM PRESSURES*

Oil	Pressure, psig		
	4500	3000	1500
O ₁	1.2890	1.153	1.197
O ₂	1.2930	1.430	1.460
O ₃	1.2830	1.350	1.250
O ₄	1.2880	1.440	1.498
Used K Values in the Program			
O ₁	1.315	1.315	
O ₃	1.370	1.370	

*The K values for Oil No. 1 were obtained by taking the average of the K values of all the runs at 4500 and 3000 psig. The K value for Oil No. 3 is the average of the K values at 3000 and 1500 psig of Oil No. 2 and Oil No. 3.

was performed in order to obtain equilibrium of the system since it was very hard for the system to reach equilibrium without that minor adjustment. After that adjustment and grouping all the other heavy components such as $C_4H_{10}^+$ at 3000 and at 1500 psig equilibrium pressure and such as $C_5H_{12}^+$ at 4500 psig, the system achieved equilibrium. These values and the adjusted ones are presented in Table 29. All the oil samples, their condensates, and their residuals were analyzed by the chromatograph and some of them by the mass spectrometer to identify the components. Oils Nos. 1, 2, 3 and 4 and their condensates and residuals obtained at 4500 psig equilibrium pressure were analyzed simultaneously by the chromatograph and the mass spectrometer. This was necessary due to the unavailability of the mass spectrometer. The cost of the mass spectrometer was high, since a long time was required to scan all the component's peaks obtained by the chromatograph. However what was needed for the program runs was obtained, and the readings of the mass spectrometer are available in Tables 30 through 41. Readings of the mass spectrometer of the original oil samples, No. 1, No. 2, No. 3 and No. 4, and their residuals and their condensates obtained from 4500 psig runs are presented in Tables 30 through 41. The mass spectrometer charts represent readings of the scanning of the peaks obtained by the chromatograph. Usually they represent M/e , mass divided by charge versus abundance; that is to say, each sample fed into the chromatograph produced component peaks

TABLE 29
K VALUES READ FROM THE CHARTS AND USED IN THE PROGRAM AT 100°F

Working Pressure:	Pressure, psig											
	1500				3000				4500			
Convergence Pressure:	4000	5000	10,000	Used in the Prog.	4000	5000	10,000	Used in the Prog.	4000	5000	10,000	Used in the Prog.
Oil No. 1												
Oil Components												
C ₁ H ₄	2.70	2.65	2.95	3.00	1.45	1.65	1.90	1.95		1.26	1.50	1.55
C ₂ H ₆	0.80	0.80	0.80	0.80	0.90	0.84	0.80	0.80		1.06	0.86	0.85
C ₃ H ₈	0.40	0.38	0.38	0.40	0.69	0.60	0.50	0.50		0.85	0.60	0.60
C ₄ H ₁₀	0.205	0.25	0.19	0.192	0.48	0.43	0.33	0.326		0.80	0.46	0.46
C ₅ H ₁₂₊	0.12	0.09	0.087		0.35	0.5	0.19			0.80	0.34	0.32
CO ₂	1.60			1.75	1.30			1.315*				1.315*
Oil No. 3 **												
CO ₂				1.75				1.37*				1.37*

*Those values were calculated for each oil separately as in Table 28 and Appen. E.

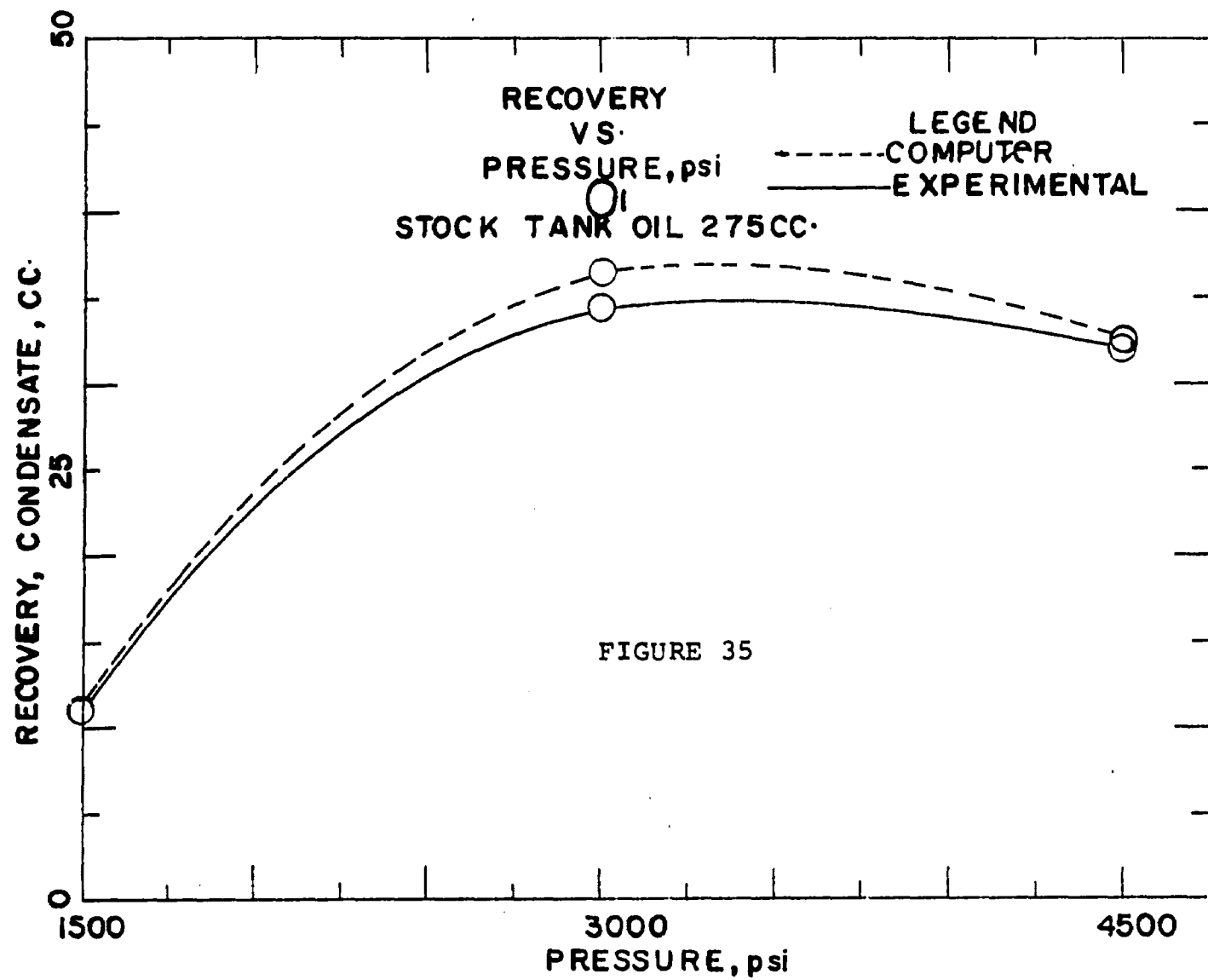
**All other values are the same as Oil No. 1.

which were then scanned one by one by the mass spectrometer. However each peak might be an isomer or a component of that sample, and when it reached the ionization chamber, the spectrometer might break it into many fragments. These fragments were scanned by the spectrometer. Its chart is called the mass spectrum which shows the M/e on the abscissa versus their relative abundance or their relative intensity as ordinate. These charts were interpreted and read as explained in References 6 and 28. However, the isomers of each component, or the fragments of these isomers, were grouped and considered to be as their normal component as indicated by their molecular weight readings. Tables 30 through 41 of the mass spectrum represent the readings of M/e obtained from the charts for each fragment. There were many fragments in each peak scanned by the spectrometer. Their relative abundance or intensity for each peak is represented by 1, 2, 3, 4 and so on. There are many peaks which might represent one isomer or one component of that sample. These are represented by the ordinate of the table, for instance, Table 30 for oil No. 1. The readings of 43, 42, 29, 27 are the M/e of the fragments obtained from peak No. 1, obtained by the chromatograph. Their relative abundance or the relative intensity of the fragments were 1, 2, 3, 4 and 5. In other words, fragments mass divided by charge $M/e = 43$ is more abundant or more intensive than the second $M/e = 42$ and so on. The ordinate of that table is the peak number obtained by the chromatograph

and fed into the mass spectrometer numbered as 1, 2, 3, 4, 5 and 6. These Tables 30 through 41 represent the readings of M/e obtained by the mass spectrometer of the original oil samples, oils Nos. 1, 2, 3, and 4 and their condensates and their residuals at 4500 psig evaporation runs. Tables 30, 31 and 32 are for O_1 , C_1A and R_1A . Tables 33, 34 and 35 represent O_2 , C_2A and R_2A . Tables 36, 37 and 38 represent O_3 , C_3A and R_3A . Tables 39, 40 and 41 represent O_4 , C_4A and R_4A . The composition of oils No. 1, No. 2, No. 3 and No. 4 as they were analyzed by the chromatograph and identified by the mass spectrum charts are presented in Tables 19, 20, 21 and 22, respectively. All the runs obtained from the chromatograph of the original oil samples, their residuals and their condensates are available in charts but they are not included in this text, since only the original oil samples compositions were required for the computer program. These mass spectrum charts are long, each one of them is about 30 to 40 feet in length. Since each peak indicated by the chromatograph was scanned by the spectrometer, usually each run in the spectrometer consumed a time between 40 and 60 minutes. Therefore they are not included in this text.

The computer program was written originally for all the oils and also for three convergence pressures, 10,000, 5000 and 4000 psig. But due to the lack of representative K values of the heavy components of oil No. 2 and oil No. 4, it was difficult for the system to reach equilibrium with the

available K values. Oils No. 2 and No. 4 with convergence pressures 4000 and 5000 were eliminated. The computer program is presented in Appendix H, and the flow chart diagram is presented in Figure 37. The K values for all the components were obtained from Reference 29 with very minor adjustment, since the heavy components were eliminated, and they have much to do with the system equilibrium. The K values of these components are presented in Table 29. The K values for carbon dioxide at 4500 and 3000 psig were not available for 10,000 psig convergence pressure, so they were calculated experimentally in a method presented in Appendix E; they are presented in Table 28. The materials fed into the program were calculated as in Appendix D and are presented in Table 27. This appendix presents calculation of these data for the 1500 psig run. The other data for other pressures, 3000 and 4500 psig, could be calculated in the same manner. The results of the computer program are also presented in Table 27, and they are plotted in Figure 35 which represents oil No. 1 and Figure 36 which represents oil No. 3. These plots represent recovery obtained after injection of the same size gas cap, obtained from the experiments at the same equilibrium pressure. The solid lines of these figures represent the recovery obtained from the experiments and are recorded in Tables 6 through 17, while the dotted lines represent the computer program results using the same size gas cap as in the experiments for each equilibrium pressure for each oil. The results



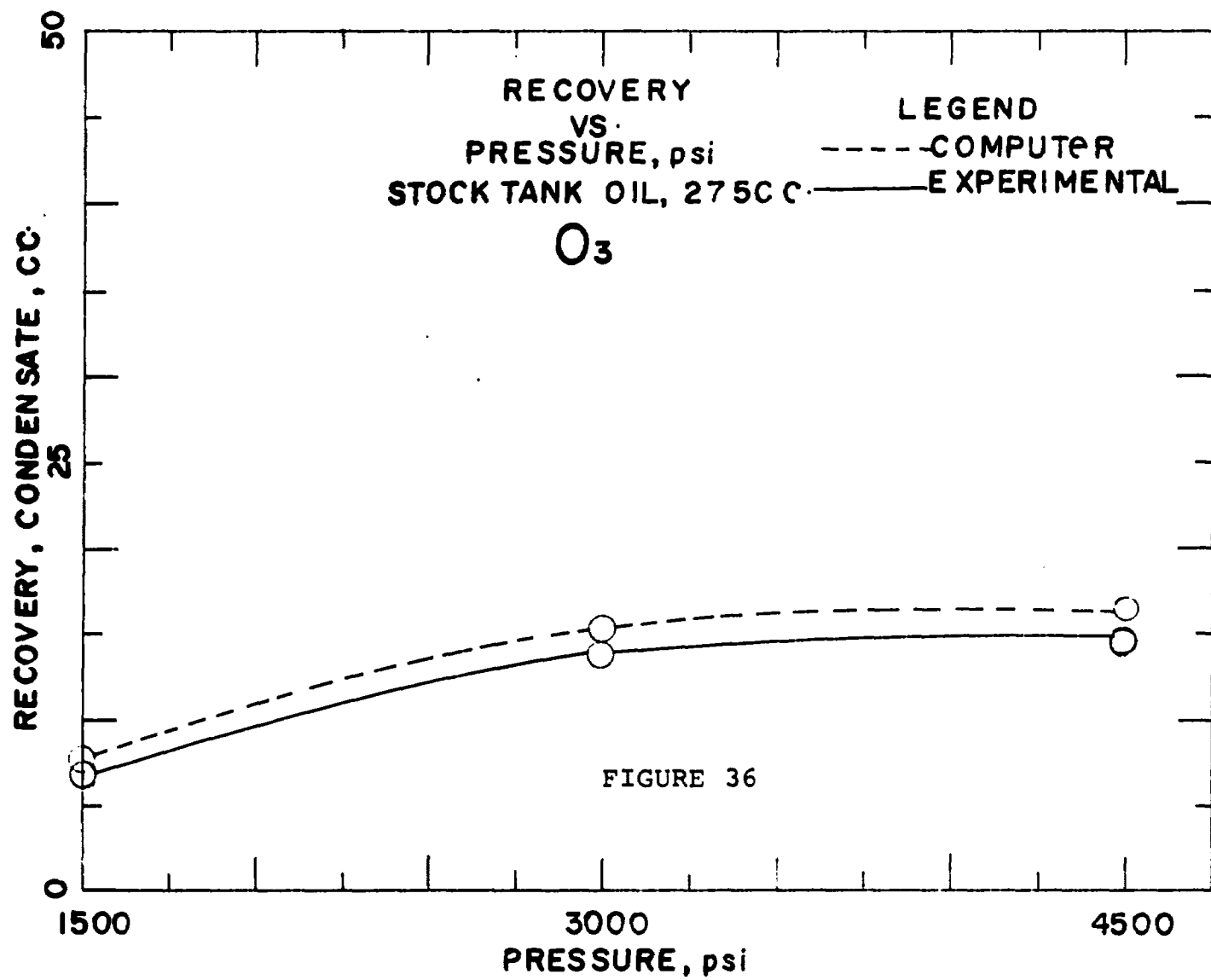
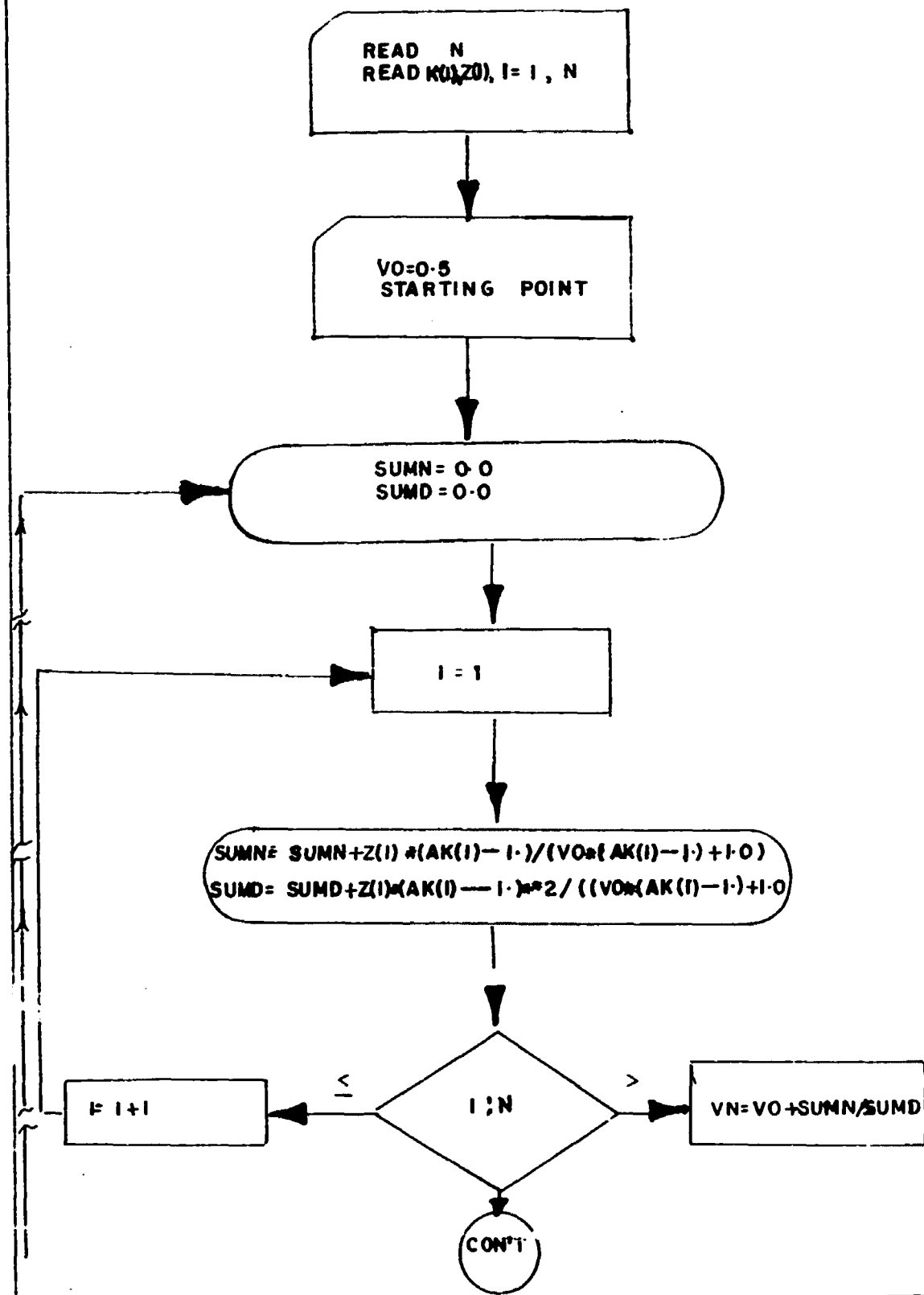
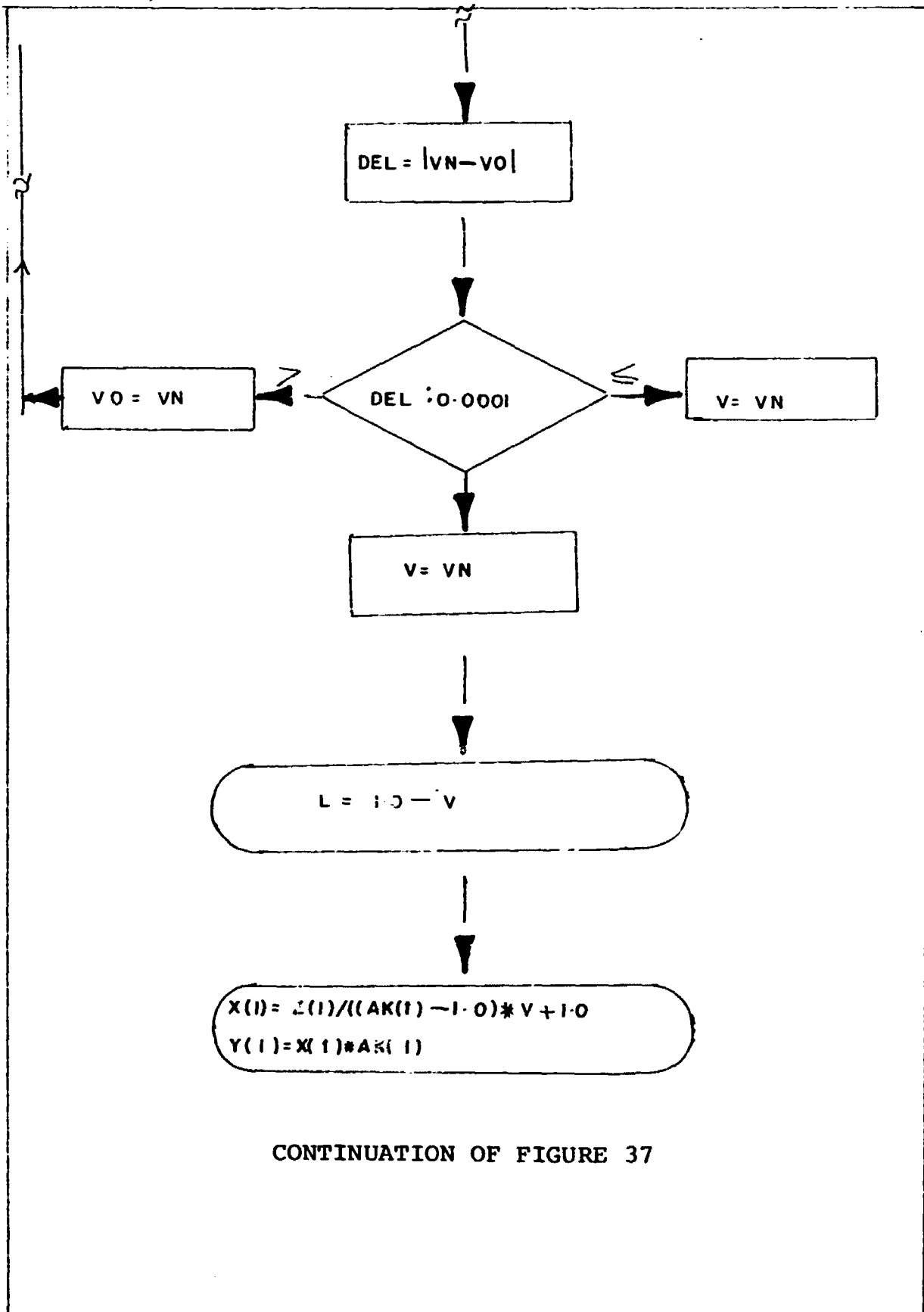


Figure 37. Flow Chart Diagram of the Computer Program.





CONTINUATION OF FIGURE 37

obtained from the computer program and those from the experiments were in very good agreement. The convergence pressure of 10,000 psig and the minor adjustments of the K values of some of the components were encouraging since they gave good results and better equilibrium than those K values at 4000 or 5000 psig convergence pressures. The latter produced no equilibrium in the system. For the same reason, the K values for carbon dioxide at 4500 and 3000 were calculated, and they were assumed for the system convergence pressure at 10,000 psig.

It was noticed from the theoretical investigation that the K values of the system components as studied before are functions of pressure, temperature, composition and convergence pressure, but it might be of interest to mention that at the same convergence pressure and at the same temperature the K values will decrease as the working pressure increases. (See Table 29 and Table 4.) At the same convergence pressure and at the same working pressure, the K values will increase as the temperature increases. At the same temperature and at the same working pressure, the K values of those components will vary in their behavior as the convergence pressure increases or decreases. This is indicated in Table 29.

It was also noticed from the calculation of this system that the K values of the hydrocarbon component C_5H_{12} which has the highest concentration in the system feed composition after carbon dioxide will control the oil recovery. Increasing

the K value of this component by a minor portion will increase the recovery by an appreciable amount, and decreasing it a little bit will decrease the oil recovery by another appreciable amount. This was noticed at all the equilibrium pressures for all oils.

Possible Errors and Their Sources

Errors may have been committed in performing these experiments. However, none of them was significant enough to change the obtained results. Some of these errors occurred in reading the gas cap volume. This volume was always obtained at the same equilibrium pressure, 1500, 3000 or 4500 psig. For instance at equilibrium pressure of 3000 psig, the starting reading of the pump at this pressure is obtained. Then after displacing all the gas cap out, the last reading is obtained again at 3000 psig. The difference between the two readings is the size of the gas cap volume.

Other sources of errors are the precision of the equipment and their calibration. Measurements of the pressure were obtained by two Bourdon tube Heise gauges, 7500 psig and 10,000 psig; both were calibrated to the nearest 10 psig. A 500 cc graduated cylinder was used to measure the oil volume. It was calibrated to the nearest 5 cc. Readings could be estimated accurately within 1 cc. The volume of the condensates were measured by 50, 25 and 1 cc graduated cylinders. Their calibration was to the nearest 1, 0.5 and 0.1 cc respectively.

The syringe used to inject liquid samples into the chromatograph was calibrated to nearest 0.1 μ liter. Reading of the Beckman thermometer to measure the freezing point in the molecular weight experiments was to the nearest 0.01 of one degree. The wet-testmeter was calibrated to the nearest 1/1000 of a cubic foot. However it was read to nearest 0.0001 cubic foot.

CHAPTER VII

CONCLUSIONS

This study made a useful contribution to the knowledge of oil recovery by carbon dioxide injection. The data collected from this investigation apply to conditions under which the experiments were performed by using the cited equipment. As a result of this study, the following conclusions were reached for the subject experimental conditions.

1. Oil recovery (condensate) is a function of the equilibrium pressure. The higher the pressure, the higher the oil recovery. The volume of oil recovered might not follow the relation that doubling the pressure will double the recovery. However, this was approximately true for the experiments.
2. Oil recovery is also a direct function of the oil API gravity. A lighter oil or an oil with a high API gravity will give a greater oil recovery than heavier oils or oils with low API gravity.
3. Oil composition is an important factor and plays a large role in controlling oil recovery. Oil with more light ends gives more oil recovery than oil with more heavy ends.

4. Oil recovery is also a function of the size of the gas cap of carbon dioxide injected. With a larger gas cap, more oil is expected to be recovered than with smaller gas cap of carbon dioxide.
5. The formation volume factor of the oil after carbon dioxide injection behaves in a way which is similar to oil recovery. The formation volume factors of these oils after carbon dioxide injection in the experiments, keeping the temperature constant, are functions of pressure, gravity, and oil composition. Injection of carbon dioxide at a higher pressure will result in a higher value of the formation volume factors. Higher formation volume factors are expected from oils with more light ends than oils with more heavy ends.
6. Oil No. 1 was the lightest in gravity and the best in composition. Oil No. 3 had a better composition than oil No. 2 and oil No. 4. Oil No. 1 and oil No. 3 gave the greatest amount of recovery and the highest formation volume factor after carbon dioxide injection. Even oil No. 3 was heavier in gravity than oil No. 2. This means that carbon dioxide injection into oils similar to No. 1 and No. 3 in composition is more promising.
7. The density of the condensate was always less than the original oil sample density and much less than the density of the residual oil left after carbon dioxide injection.

8. The densities of the condensates and their residual oils were functions of the equilibrium pressure. They increase as the equilibrium pressure increases, and they decrease as the equilibrium pressure decreases.
9. The effect of carbon dioxide on the oil was to produce condensates with lower densities than the original oils and with much lower densities than their residuals.
10. The effect of carbon dioxide on oil molecular weight was to produce a condensate of lower molecular weight than the original oil and of much lower molecular weight than its residual.
11. The molecular weights of these condensates and their residuals were functions of the equilibrium pressure. The molecular weights increase as the pressure increases, and they decrease as the pressure decreases.
12. It might be expected that a lighter gravity oil has lower molecular weight. This is not always true, since oil No. 3 is heavier than oil No. 2, but it has a lower molecular weight than oil No. 2. Even its condensates were of lower molecular weight than the condensates of oil No. 2, at the same pressures.
13. A certain minimum amount of carbon dioxide should be injected in order to produce some recoverable oil. The amount of the carbon dioxide to be injected should be more than 80 mole percent of the total feed into the system.

14. The light ends which might be lost during evaporation and condensation were more prevalent for oils of lighter gravity and for those oils which have a better composition. Those losses were functions of the equilibrium pressure; at higher pressures, more loss was experienced.
15. Composition and gravity of the oil are the two important factors (keeping the pressure, temperature, number of moles of oil fed and the size of the gas cap constant) for forecasting the amount of condensate to be recovered and the carbon dioxide gas to be dissolved or to be liberated.
16. The recovery results obtained from the theoretical investigation were in very good agreement with the recovery results obtained from the experiments.
17. The K values for carbon dioxide calculated from experimental equilibrium pressure gave encouraging recovery results which were in good agreement with those obtained from the actual run.
18. In spite of all the previous advantages of carbon dioxide such as reduction of oil viscosity, oil surface tension, good solubility, swelling, etc., the property of the low vapor pressure of carbon dioxide might be one of the most important factors in the injection recovery process.

TABLE 30
MASS SPECTROMETER READINGS M/e, O₁

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading		
		1	2	3	4	5	6	7			
Peaks were scanned by mass spectrometer and obtained by the chromatograph	1	43	42	29	27				58	C ₄	H ₁₀
	2	43	42	41	27	29			72	C ₅	H ₁₂
	3	43	42	41	27	57			72	C ₅	H ₁₂
	4	43	42	41	29	27			86	C ₆	H ₁₄
	5	43	57	41	29	41			86	C ₆	H ₁₄
	6	43	41	57	29	56			86	C ₆	H ₁₄
	7	43	29	57					86	C ₆	H ₁₄
	8	43	56	41	42	85	29	27	86	C ₆	H ₁₄
	9	43	70	57	56	71	41		98	C ₇	H ₁₆
	10	56	71	41	55	97	83		98	C ₇	H ₁₆
	11	43	41	57	71	55	29	70	98	C ₇	H ₁₆
	12	81	55	41	97				98	C ₇	H ₁₆
	13	43	57	70	41	71			114	C ₈	H ₁₈
	14	97	55	41	43				114	C ₈	H ₁₈
	15	43	57	85	41	29	71		114	C ₈	H ₁₈
	16	81	41	55	43	71			132	C ₉	H ₂₀
	17	43	57	81					140	C ₁₀	H ₂₂
	18	43	57	71	81				148	C ₁₀	H ₂₂
	19	57	43	41	29	27			146	C ₁₀	H ₂₂
	20	55	97	41	43				142	C ₁₀	H ₂₂
	21	43	57	41	56	85	29		148	C ₁₀	H ₂₂
	22	43	57	55	41				156	C ₁₁	H ₂₄
	23	57	43	55	41	81			156	C ₁₁	H ₂₄
	24	57	71	43	41	55			156	C ₁₁	H ₂₄
	25	43	57	55	100				156	C ₁₁	H ₂₄

TABLE 30--Continued

Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading	
	1	2	3	4	5	6	7		
26	57	43	71	85				156	C ₁₁ H ₂₄
27	57	43	71	97				156	C ₁₁ H ₂₄
28 HT*	55	97	103					156	C ₁₁ H ₂₄
29	43	57	41	71	85	29	27	156	C ₁₁ H ₂₄
30	43	57	41	71	85	29	27	156	C ₁₁ H ₂₄
31	55	41	69	57	71			156	C ₁₁ H ₂₄
32	43	57	41	71	29			156	C ₁₁ H ₂₄
33	43	41	57	29	55			166	C ₁₂ H ₂₆
34	55	41	81	43	29			166	C ₁₂ H ₂₆
35	57	41	43	55	29			166	C ₁₂ H ₂₆
36	43	57	41	29	55	71		180	C ₁₃ H ₂₈
37	43	57	41	29	55	71		190	C ₁₄ H ₃₀
38	43	57	41	55	71	29		190	C ₁₄ H ₃₀
39	41	43	57	55	29			190	C ₁₄ H ₃₀
40	41	43	57	55	71	69		214	C ₁₅ H ₃₂
41	41	57	55	43	71	69	29	214	C ₁₅ H ₃₂
42	43	41	57	55	71	29		214	C ₁₅ H ₃₂
43	41	57	55	43	69	81	71	226	C ₁₆ H ₃₄
44	43	41	57	55	29	71		226	C ₁₆ H ₃₄
45	43	41	55	57	69	71		226	C ₁₆ H ₃₄
46	43	57	41	55	71	29		226	C ₁₆ H ₃₄

Peaks were scanned by mass spectro-
meter and obtained by chromatograph.

*High temperature.

TABLE 31
MASS SPECTROMETER READINGS M/e, C₁A

Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number								Last Mole. Wt. Reading		
	1	2	3	4	5	6	7	8			
Peaks were scanned by mass spectrometer and obtained by the chromatograph.	2	43	57	41	69	29	56	55	71	126	C ₉ H ₂₀
	3	55	97	41	56	69	85			132	C ₉ H ₂₀
	4	43	85	41	56	71	55	29	69	126	C ₉ H ₂₀
	5	43	55	57	41	85	56	42		132	C ₉ H ₂₀
	6	43	57	41	71	42	85			140	C ₁₀ H ₂₀
	7	57	43	41	29	97				140	C ₁₀ H ₂₀
	8	43	57	41	29	85	71			136	C ₁₀ H ₁₄
	9	43	55	57	42	69				134	C ₁₀ H ₁₄
	10	43	55	85	41	57				132	C ₁₀ H ₂₀
	11	57	43	42	55	97				132	C ₁₀ H ₁₄
	12	43	57	41	56	55	69			132	C ₁₀ H ₁₄
	13	55	41	56	90	70	82			140	C ₁₀ H ₂₀
	14	43	57	41	71	29	27			140	C ₁₀ H ₂₀
	15	43	57	71	42	55	69			140	C ₁₀ H ₂₀
	16	55	69	41						132	C ₁₀ H ₁₄
	17	43	57	71	41	55	69			136	C ₁₀ H ₁₄
	18	HT*	43	41	57	71	29	85		136	C ₁₀ H ₁₄
	19		43	41	57	55	71	69		146	C ₁₁ H ₁₆
	20		43	41	57	55	71	29	85	146	C ₁₁ H ₁₆
	21		43	41	57	55	29	27		150	C ₁₁ H ₁₆
	22		43	41	57	55	69	29		150	C ₁₁ H ₁₆
	23		43	41	57	55	61	71		160	C ₁₂ H ₁₈
	24		43	41	57	55	29	69	71	166	C ₁₂ H ₂₄
	25		43	41	57	55	71	29		166	C ₁₂ H ₂₄
	26		43	41	57	55	71	29	69	188	C ₁₃ H ₂₈
										200	C ₁₄ H ₃₀

*High Temperature.

TABLE 32
MASS SPECTROMETER READINGS M/e, R₁A

Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
	1	2	3	4	5	6		
4	43	55	41	67	56	68	156	C ₁₁ H ₂₄
5	43	41	56	55	65	64	156	C ₁₁ H ₂₄
6	80	53	41	54	97		156	C ₁₁ H ₂₄
7	43	57	41	70	71		156	C ₁₁ H ₂₄
8	55	97	41	111	43		156	C ₁₁ H ₂₄
9	43	57	85	71	55		152	C ₁₁ H ₂₄
10	57	41	83	43	69		150	C ₁₁ H ₂₄
11	43	57	84	71			156	C ₁₁ H ₂₄
12	55	47	43				152	C ₁₁ H ₂₄
13	43	57	41	55	71		156	C ₁₁ H ₂₄
14	41	57	43				162	C ₁₁ H ₂₄
15	43	57	69				150	C ₁₁ H ₂₄
16								
17	43	57	41	71	85		150	C ₁₁ H ₂₄
18	HT* 43	71	57	29	41		156	C ₁₁ H ₂₄
19	41	43	57	55	71		156	C ₁₁ H ₂₄
20	55	41	70	29	56		156	C ₁₁ H ₂₄
21	41	57	43	39	71	29	156	C ₁₁ H ₂₄
22	41	55	43	39	29	27	156	C ₁₁ H ₂₄
23	41	43	55	57	29	27	156	C ₁₁ H ₂₄
24	41	43	29	57	29	27	170	C ₁₂ H ₂₄
25	41	43	55	29	27		170	C ₁₂ H ₂₄

*High temperature.

TABLE 32--Continued

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
		1	2	3	4	5	6		
Peaks scanned by mass spectrometer, obtained by chro- matograph.	26	41	43	55	29	57	27	170	C ₁₂ H ₂₄
	27	41	43	55	29	57		176	C ₁₃ H ₂₀
	28	41	43	55	57	29	27	176	C ₁₃ H ₂₀
	29	41	43	55	29	57	27	198	C ₁₄ H ₃₀
	30	41	55	43	29	57		198	C ₁₄ H ₃₀
	31	41	43	55	29	57	29	212	C ₁₅ H ₃₂
	32	41	55	43	57	29		212	C ₁₅ H ₃₂
	33	41	43	55	57	29		214	C ₁₅ H ₃₂
	34	43	41	55	57	29		214	C ₁₅ H ₃₂
								214	C ₁₅ H ₃₂

TABLE 33
MASS SPECTROMETER READINGS M/e, O₂

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
		1	2	3	4	5	6		
Peaks were scanned by mass spectrometer and obtained by the chromatograph.	1							148	C ₁₀ H ₂₂
	2							148	C ₁₀ H ₂₂
	3							148	C ₁₀ H ₂₂
	4	55	41	43				148	C ₁₀ H ₂₂
	5	69	55	53	41	43		148	C ₁₀ H ₂₂
	6	82	53	41	97	55	57	148	C ₁₀ H ₂₂
	7	69	55	53	71	41		148	C ₁₀ H ₂₂
	8	96	55	111	82	69	41	142	C ₁₀ H ₂₂
	9	96	55	111	69	41		142	C ₁₀ H ₂₂
	10	111	69	82	55	41	56	142	C ₁₀ H ₂₂
	11	93	111	43	57			148	C ₁₀ H ₂₂
	12	55	69	95	85	114		148	C ₁₀ H ₂₂
	13	97	69	55	124			148	C ₁₀ H ₂₂
	14	55	82	97	57			148	C ₁₀ H ₂₂
	15	55	69	85	97			156	C ₁₁ H ₂₄
	16	57	69	55	97			156	C ₁₁ H ₂₄
	17	69	111	55	57			156	C ₁₁ H ₂₄
	18	111	55	69	96			164	C ₁₂ H ₂₆
	19	97	55	69	82			164	C ₁₂ H ₂₆
	20	57	43	55	69			164	C ₁₂ H ₂₆
	21 HT*	69	55	119	82	117		180	C ₁₃ H ₂₈
	22	69	57	82	55	41	43	180	C ₁₃ H ₂₈

*High temperature

TABLE 33--Continued

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
		1	2	3	4	5	6	7	
Peaks scanned by mass spectrometer, obtained by chroma- tograph.	23	69	55	41	82	96	153		C ₁₃ H ₂₈
	24	55	41	69	131	43	57		C ₁₃ H ₂₈
	25	69	55	82	41	85	57		C ₁₃ H ₂₈
	26	69	57	55	81	82			C ₁₄ H ₃₀
	27	69	55	57	96	41	43		C ₁₄ H ₃₀
	28	55	69	82	43	41			C ₁₅ H ₃₂
	29	55	69	41	57	43			C ₁₅ H ₃₂
	30	55	57	69	41	82	43		C ₁₅ H ₃₂
	31	55	69	158	96	57	43	41	C ₁₆ H ₃₄
	32	57	71	55	43	41	69	82	C ₁₆ H ₃₄

TABLE 34
MASS SPECTROMETER READINGS M/e, C₂A

Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading	
	1	2	3	4	5	6	7		
1									
2	97	55	41	111	69			148	C ₁₀ H ₂₂
3	97	55	69	111	55			156	C ₁₁ H ₂₄
4	111	69	55	81	69	56		156	C ₁₁ H ₂₄
5	43	69	111	81	57			156	C ₁₁ H ₂₄
6	55	69	56	41	70			156	C ₁₁ H ₂₄
7	97	55	69	43	41			156	C ₁₁ H ₂₄
8	55	43	57	41	81			170	C ₁₂ H ₂₆
9	55	57	43	85	41			180	C ₁₂ H ₂₆
10	69	57	55	41	43			180	C ₁₂ H ₂₆
11	69	55	70	41	111			180	C ₁₂ H ₂₆
12	55	69	96	41	96			178	C ₁₂ H ₂₆
13	55	96	69	81	41	43		178	C ₁₂ H ₂₆
14	57	69	55	41	104			178	C ₁₂ H ₂₆
15	57	55	43	41	69	71		184	C ₁₃ H ₂₈
16	43	55	114	41				184	C ₁₃ H ₂₈
17 HT*	112	69	55	43	57			180	C ₁₃ H ₂₈
18	69	55	57	41	43			189	C ₁₃ H ₂₈
19	41	55	43	69	81	80		189	C ₁₃ H ₂₈
20	41	69	43	57	55			189	C ₁₃ H ₂₈
21	41	55	69	57	85	81		190	C ₁₃ H ₂₈
22	41	55	69	57	43	81		194	C ₁₄ H ₃₀
23	41	55	43	57	69	29	27	202	C ₁₄ H ₃₀

*High temperature.

TABLE 34--Continued

Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading	
	1	2	3	4	5	6	7		
24	41	43	55	69	57	29	67	214	C ₁₅ H ₃₂
25	43	41	55	57	69	29	71		C ₁₅ H ₃₂

TABLE 35
MASS SPECTROMETER READINGS M/e, R₂A

Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
	1	2	3	4	5	6		
1								
2								
3							142	C ₁₀ H ₂₂
4							142	C ₁₀ H ₂₂
5							142	C ₁₀ H ₂₂
6	43	69	71	55			142	C ₁₀ H ₂₂
7	55	97	111	69			156	C ₁₁ H ₂₄
8	97	55	69	82			156	C ₁₁ H ₂₄
9	111	69	55	81	41		156	C ₁₁ H ₂₄
10	69	82	43	111			156	C ₁₁ H ₂₄
11	55	97	69	125			156	C ₁₁ H ₂₄
12	57	97	69	85			156	C ₁₁ H ₂₄
13	82	55	415				156	C ₁₁ H ₂₄
14	55	82	57	95			156	C ₁₁ H ₂₄
15	57	69	43	41			156	C ₁₁ H ₂₄
16	69	111	55				156	C ₁₁ H ₂₄
17	55	69	97	81			160	C ₁₁ H ₂₄
18	55	69	97	111			170	C ₁₂ H ₂₆
19	55	69	82	111			170	C ₁₂ H ₂₆
20							170	C ₁₂ H ₂₆
21	69	55	119	41			170	C ₁₂ H ₂₆
22	69	55	41	82	57		170	C ₁₂ H ₂₆
23	55	69	41	97	119		170	C ₁₂ H ₂₆

Peaks were scanned by mass spectrometer
and obtained by the chromatograph.

TABLE 35--Continued

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
		1	2	3	4	5	6		
Peaks scanned by mass spectrometer, obtained by chroma- tograph.	24	55	69	81	41	94		184	C ₁₃ H ₂₈
	25	69	55	57	41	81		184	C ₁₃ H ₂₈
	26	69	55	41	57	81		184	C ₁₃ H ₂₈
	27	55	69	41	81	95		184	C ₁₃ H ₂₈
	28	69	55	41	43	82	81	184	C ₁₃ H ₂₈
	29	55	69	41	57	82	81	198	C ₁₄ H ₃₀
	30	55	69	41	43	95	82	198	C ₁₄ H ₃₀
	31	41	55	69	57	43	82	214	C ₁₅ H ₃₂
	32	55	57	69	82	41	43	214	C ₁₅ H ₃₂
	33	55	57	43	41	71	69		

TABLE 36
MASS SPECTROMETER READINGS M/e, O₃

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number								Last Mole. Wt. Reading		
		1	2	3	4	5	6	7	8			
Peaks were scanned by mass spectrometer and obtained by the chromatograph.	1	43	29	41	27	39				58	C ₄	H ₁₀
	2	43	42	41	29	27				58	C ₄	H ₁₀
	3	43	42	41	57	71	29	27		72	C ₅	H ₁₂
	4	43	41	57	29	27				72	C ₅	H ₁₂
	5	43	56	57	41	71	29	27		86	C ₆	H ₁₄
	6	57	43	41	56	85	29	27		86	C ₆	H ₁₄
	7	55	41	43	69					86	C ₆	H ₁₄
	8	43	55	57	81	41	42	29	27	100	C ₇	H ₁₆
	9	43	55	41	69	57	29	27	71	100	C ₇	H ₁₆
	10	82	55	97	41	57	27	29		114	C ₈	H ₁₈
	11	43	57	41	70	70	29	27		114	C ₈	H ₁₈
	12	97	55	111	56					114	C ₈	H ₁₈
	13	43	41	55	57	85				114	C ₈	H ₁₈
	14	55	69	111	41	43				128	C ₉	H ₂₀
	15	43	57	41	29	27				128	C ₉	H ₂₀
	16	55	82	97	69	56				142	C ₁₀	H ₂₂
	17	42	43	57	55					142	C ₁₀	H ₂₂
	18	41	43	57	56	55				142	C ₁₀	H ₂₂
	19	57	71	56	55	43	41			142	C ₁₀	H ₂₂
	20	57	43	71	41					142	C ₁₀	H ₂₂
	21	43	69	57	56	60				142	C ₁₀	H ₂₂
	22	55	57	41	41					142	C ₁₀	H ₂₂
	23									142	C ₁₀	H ₂₂

TABLE 36--Continued

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading
		1	2	3	4	5	6	7	
Peaks were scanned by mass spectro- meter and obtained by chromatograph.	24	57	43	71	69	41			C ₁₀ H ₂₂
	25	71	55	43	41				C ₁₀ H ₂₂
	26								C ₁₀ H ₂₂
	27	43	57	71	69	41	55		C ₁₁ H ₂₄
	28	69	55	41	97	43			C ₁₁ H ₂₄
	29	57	55	43	41	85			C ₁₂ H ₂₆
	30	55	41	82	69	57			C ₁₂ H ₂₆
	31	57	43	69	55	56			C ₁₂ H ₂₆
	32	57	43	41	55	71	69		C ₁₃ H ₂₈
	33	57	43	41	69	82			C ₁₃ H ₂₈
	34	69	55	41	57	43			C ₁₃ H ₂₈
	35	55	41	69	57	43			C ₁₃ H ₂₈
	36	41	69	55	57	43			C ₁₄ H ₃₀
	37	41	55	57	43	69			C ₁₄ H ₃₀
	38	41	43	55	57	81			C ₁₄ H ₃₀
	39	57	43	41	55	95			C ₁₅ H ₃₂
	40	57	55	41	43	95			C ₁₅ H ₃₂
	41	41	55	69	57	43			C ₁₅ H ₃₂
	42	43	57	71	41	55	82		C ₁₆ H ₃₄
	43	57	43	55	69	41			C ₁₆ H ₃₄

*High temperature.

TABLE 37
MASS SPECTROMETER READINGS M/e, C₃A

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading		
		1	2	3	4	5	6	7			
Peaks were scanned by the mass spectro- meter and obtained by chromatograph.	1	43	57	41	40	29			72	C ₅	H ₁₂
	2	57	56	43	71	55	56		86	C ₆	H ₁₄
	3	57	43	56	43	55	85		86	C ₆	H ₁₄
	4	55	71	41	82				86	C ₆	H ₁₄
	5	43	55	57	56	85			86	C ₆	H ₁₄
	6	43	41	56	71	57	69		100	C ₇	H ₁₆
	7	82	55	97	41	56	57	71	112	C ₈	H ₁₈
	8	43	57	71	42	71	41		114	C ₈	H ₁₈
	9	97	55	111	56	41	69		128	C ₉	H ₂₀
	10	41	43	85	57	56	71	29	128	C ₉	H ₂₀
	11	43	57	71	41	42	56	85	142	C ₁₀	H ₂₂
	12	43	57	52	95	69	55	111	142	C ₁₀	H ₂₂
	13	55	147	69	41	56	82		42	C ₁₀	H ₂₂
	14	43	57	41	85	71	29		142	C ₁₀	H ₂₂
	15	55	81	43	57	41	66		142	C ₁₀	H ₂₂
	16	81	57	55	43	41	71	97	156	C ₁₁	H ₂₄
	17	57	43	97	69	55	56	41	156	C ₁₁	H ₂₄
	18	43	70	57	69	56	55	41	156	C ₁₁	H ₂₄
	19	55	41	81	57	43	69	97	156	C ₁₁	H ₂₄
	20	55	70	96	41	104	56	69	156	C ₁₁	H ₂₄
	21	43	57	71	41	29	55	56	156	C ₁₁	H ₂₄
	22	43	57	71	70	41	55	56	156	C ₁₁	H ₂₄
	23	57	43	69	55	41	71		156	C ₁₁	H ₂₄

TABLE 37--Continued

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number								Last Mole. Wt. Reading	
		1	2	3	4	5	6	7	8		
Peaks were scanned by mass spectrometer, obtained by chromato- graph.	24	69	55	57	41	43	71	70	69	156	C ₁₁ H ₂₄
	25	43	57	71	41	29	85	55		156	C ₁₁ H ₂₄
	26	55	41	69	81	41	57	43		170	C ₁₂ H ₂₆
	27	43	57	55	41	71	69	81		170	C ₁₂ H ₂₆
	28	55	41	41	57	69	29	71		170	C ₁₂ H ₂₆
	29	41	43	57	55	71	69	29		170	C ₁₂ H ₂₆
	30	41	43	55	57	71	69	29		184	C ₁₃ H ₂₈
	31	41	57	55	43	69	29	81		184	C ₁₃ H ₂₈
	32	41	55	43	57	29	69			184	C ₁₃ H ₂₈
	33	41	43	55	57	69	29			198	C ₁₄ H ₃₀
	34	41	43	55	57	69	71	29		198	C ₁₄ H ₃₀
	35	43	55	57	41	69	71	29		198	C ₁₄ H ₃₀

*High temperature.

TABLE 38
MASS SPECTROMETER READINGS M/e, R₃A

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading
		1	2	3	4	5	6	7	
Peaks were scanned by mass spectrometer and obtained by the chromatograph.	1								
	2								
	3	43	41	57	55				C ₅ H ₁₂
	4								C ₅ H ₁₂
	5								C ₅ H ₁₂
	6	43	55	57	41	81			C ₆ H ₁₂
	7	43	41	55	57	71	69		C ₆ H ₁₂
	8	82	97	55	57	41			C ₆ H ₁₂
	9	43	57	69	71	97			C ₇ H ₁₆
	10								C ₈ H ₁₈
	11	43	85	57	71	55	41		C ₈ H ₁₈
	12	111	69	55	82				C ₈ H ₁₈
	13	43	57	41	71				C ₈ H ₁₈
	14	85	97	43					C ₈ H ₁₈
	15	43	57	85	69	41			C ₉ H ₂₀
	16	57	43	41	71				C ₉ H ₂₀
	17	57	97	55	43	41			C ₉ H ₂₀
	18	57	55	97	41	43			C ₉ H ₂₀
	19	69	41	43	57	55			C ₉ H ₂₀
	20								C ₉ H ₂₀
	21								C ₉ H ₂₀
	22	43	57	41	29				C ₁₀ H ₂₂
	23	57	71	43	41				C ₁₀ H ₂₂

TABLE 38--Continued

		Relative Abundance of the Fragments, Decreases in Intensity at Higher Number									
Peak Number		1	2	3	4	5	6	7	Last Mole. Wt. Reading		
Peaks were scanned by mass spectrometer and obtained by the chromatograph.	24								142	C ₁₀ H ₂₂	
	25	HT*	69	125	55	57	43	41	153	156	C ₁₁ H ₂₄
	26		57	43	55	71	69			156	C ₁₁ H ₂₄
	27		55	69	57	81	95			156	C ₁₁ H ₂₄
	28		57	43	55	41	71			170	C ₁₂ H ₂₆
	29		43	57	41	55	29	71		170	C ₁₂ H ₂₆
	30		57	43	69	41	95			170	C ₁₂ H ₂₆
	31		69	55	41	85	57			184	C ₁₃ H ₂₈
	32		41	57	55	69	71			184	C ₁₃ H ₂₈
	33		57	41	43	55	69			184	C ₁₃ H ₂₈
	34		41	57	69	55	43			184	C ₁₃ H ₂₈
	35		57	55	43	71	41			198	C ₁₄ H ₃₀
	36		57	41	43	55	69			198	C ₁₄ H ₃₀
	37		57	43	41	55	69	71		212	C ₁₅ H ₃₂
	38		57	43	55	41	69	71		212	C ₁₅ H ₃₂
	39		57	71	43	71	69	41		226	C ₁₆ H ₃₄
	40		43	55	57	41	71			226	C ₁₆ H ₃₄

*High temperature

TABLE 39
MASS SPECTROMETER READINGS M/e, O₄

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
		1	2	3	4	5	6		
Peaks were scanned by mass spectro- meter and obtained by chromatograph.	1							170	C ₁₂ H ₂₆
	2							170	C ₁₂ H ₂₆
	3							170	C ₁₂ H ₂₆
	4							170	C ₁₂ H ₂₆
	5							170	C ₁₂ H ₂₆
	6							170	C ₁₂ H ₂₆
	7							170	C ₁₂ H ₂₆
	8							170	C ₁₂ H ₂₆
	9							170	C ₁₂ H ₂₆
	10							170	C ₁₂ H ₂₆
	11							170	C ₁₂ H ₂₆
	12							170	C ₁₂ H ₂₆
	13							180	C ₁₃ H ₂₈
	14							180	C ₁₃ H ₂₈
	15							180	C ₁₃ H ₂₈
	16							180	C ₁₃ H ₂₈
	17							180	C ₁₃ H ₂₈
	18	HT*	69	55	109	81	41	180	C ₁₃ H ₂₈
	19		81	69	55	95	41	180	C ₁₃ H ₂₈
	20		69	55	81	41	95	180	C ₁₃ H ₂₈
	21		55	69	41	81	95	180	C ₁₃ H ₂₈

*High temperature.

TABLE 39--Continued

		Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
		1	2	3	4	5	6		
Peaks were scanned by mass spectro- meter, obtained by chromatograph.	24	41	55	69	81	95		190	C ₁₄ H ₃₀
	25	55	43	69	95	81		202	C ₁₅ H ₃₂
	26	55	69	41	81	95		202	C ₁₅ H ₃₂
	27	55	41	69	43	57		214	C ₁₆ H ₃₄
	28	55	41	69	95	57	43	214	C ₁₆ H ₃₄
	29	55	41	69	43	81		214	C ₁₆ H ₃₄
	30	55	57	43	41	85	81	226	C ₁₇ H ₃₆
	31	55	57	69	41	43	81	226	C ₁₇ H ₃₆
	32	55	43	41	69	81	95	226	C ₁₇ H ₃₆

TABLE 40
MASS SPECTROMETER READINGS M/e, C₄A

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading			
		1	2	3	4	5	6			7	
Peaks were scanned by mass spectro- meter and obtained by the chromato- graph.	1	55	82	139	43	57			170	C ₁₂ H ₂₆	
	2	69	111	55	70				170	C ₁₂ H ₂₆	
	3	81	69	83	57	55			170	C ₁₂ H ₂₆	
	4	81	69	83	57	55	41		170	C ₁₂ H ₂₆	
	5	69	125	83	81	55	57		190	C ₁₃ H ₂₈	
	6	114	69	83	55	41	43		190	C ₁₃ H ₂₈	
	7	69	55	114	82	57	56	57	190	C ₁₃ H ₂₈	
	8	69	55	41	83	43		41	190	C ₁₃ H ₂₈	
	9	69	55	111	83	110	95		190	C ₁₃ H ₂₈	
	10	69	83	139	55	57	41	94	189	C ₁₃ H ₂₈	
	11	69	83	94	55	139	41		189	C ₁₃ H ₂₈	
	12	94	69	55	41	8	109		190	C ₁₃ H ₂₈	
	13	69	81	109	95	82	55	57	204	C ₁₄ H ₃₀	
	14	95	69	80	55	82			204	C ₁₄ H ₃₀	
	15	95	69	80	55	121	109		204	C ₁₄ H ₃₀	
	16	95	69	82	55	57			214	C ₁₅ H ₃₂	
	17	HT*	69	55	41	109	83	81	214	C ₁₅ H ₃₂	
	18		95	41	69	55	81	109	214	C ₁₅ H ₃₂	
	19		95	41	69	55	81	83	109	214	C ₁₅ H ₃₂
	20		41	55	69	81	95	109		214	C ₁₅ H ₃₂
	21		41	55	69	95	81	43		214	C ₁₅ H ₃₂

*High temperature.

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TABLE 40--Continued

Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number							Last Mole. Wt. Reading	
	1	2	3	4	5	6	7		
22	41	55	69	43	57	81	95	214	C ₁₅ H ₃₂
23	41	55	69	43	95	81	29	214	C ₁₅ H ₃₂
24	41	55	69	43	57	81	29	226	C ₁₆ H ₃₄
25	41	55	43	69	29	71	81	226	C ₁₆ H ₃₄
26	43	41	55	57	69	71	29	226	C ₁₆ H ₃₄

TABLE 41
MASS SPECTROMETER READINGS M/e, R₄A

	Peak Number	Relative Abundance of the Fragments, Decreases in Intensity at Higher Number						Last Mole. Wt. Reading	
		1	2	3	4	5	6		
Peaks were scanned by mass spectrometer and obtained by the chromatograph.	1								C ₁₃ H ₂₈
	2								C ₁₃ H ₂₈
	3								C ₁₃ H ₂₈
	4								C ₁₃ H ₂₈
	5								C ₁₃ H ₂₈
	6								C ₁₃ H ₂₈
	7								C ₁₃ H ₂₈
	8								C ₁₃ H ₂₈
	9								C ₁₃ H ₂₈
	10								C ₁₃ H ₂₈
	11								C ₁₃ H ₂₈
	12								C ₁₃ H ₂₈
	13	HT*	69	55	81	41			C ₁₃ H ₂₈
	14		81	69	95	55	109		C ₁₃ H ₂₈
	15		95	81	41	55	69		C ₁₄ H ₃₀
	16		69	81	95	41	109		C ₁₄ H ₃₀
	17		69	95	55	41	81		C ₁₄ H ₃₀
	18		69	55	95	109	41		C ₁₄ H ₃₀
	19		55	69	41	95	81		C ₁₄ H ₃₀
	20		69	57	41	55	43		C ₁₄ H ₃₀
	21		69	82	55	57	95	41	C ₁₅ H ₃₂
	22		57	69	55	81	43		C ₁₅ H ₃₂
	23		55	43	69	95	57	95	C ₁₆ H ₃₄
	24		55	57	69	81	43	95	C ₁₇ H ₃₆

*High temperature.

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APPENDICES

APPENDIX A

CHROMATOGRAPH AND MASS SPECTROMETER

Chromatograph

The term "chromatograph" was originally applied to the separation of colored plant pigments by selective absorption. The separating principle is that of selective absorption in columns packed with a solid absorbent or with a liquid solvent supported on inert packing. It is a logical supplement to distillation methods first disclosed in 1941 by J. P. Martin. Twett used glass tubes filled with calcium carbonate. The mixed pigments were added to the top of the column and eluted (i.e., leached out or washed) through the column with a suitable solvent. Each of the various pigments moved through the column at different rates, depending on its affinity for calcium carbonate, resulting in the development of various color bands. Each band contained a different pigment, and the height of each band was proportional to the quantity of pigment present in the original sample.

Chromatography is now defined as those processes which allow the resolution of mixtures by effecting the separation of some or all of their components into certain zones or phases different from those in which they are originally present,

irrespective of the force or forces causing the substance to move from one phase to another. It is a method which consists of carrying a mixture through a column by means of a carrier gas. The different affinity of the components for the column packing (called the stationary phase) causes the components to travel at different rates through the column. They arrive at the column exit separately where they are measured by suitable detectors. Recordings obtained by measuring the detector output result in a series of peaks in which their locations or characteristic component speeds provide the qualitative information. Their heights and areas can be used for determining percentage concentrations. Basically, chromatography consists of a two phase system. One phase is fixed and is termed the static or stationary phase. It might be either a solid (absorption chromatograph) or a liquid held by a solid (partition chromatograph), and it may be contained in a column, or it may be in the form of strips or sheets of filter paper. The other phase is mobile and is termed the moving or mobile phase. This phase may be a gas, liquid, dissolved solid or colloidal solution. In all cases, the moving phase contains the sample. Phase equilibrium occurs between the sample components, the moving phase and the stationary phase. The sample components are then distributed or partitioned between the stationary phase and the moving phase. For different techniques, there will be a difference in the intensity of the force by which the stationary phase tends

to hold each of the sample components, whether the nature of this force be due to absorption, solubility, chemical bonding, or molecular filtration. The sample components will tend to become separated by repeated distribution between the stationary and moving phases as they are moved down the length of the chromatographic column. This is very similar to the operation of a distillation column where materials are separated on the basis of a difference in boiling points. Chromatography can be classified by its static and moving phases. If the moving phase is gas or liquid and the static phase is solid, the classifications are gas-solid chromatography (or gas adsorption chromatography) and adsorption chromatography (or liquid adsorption chromatography), respectively. If the static phase is liquid-held-by-solid rather than solid, then the classifications become gas-liquid chromatography (or gas-liquid partition chromatography) and partition chromatography (or liquid-liquid chromatography), respectively. The other classification is based on the method of removing the sample components from the column. Three famous methods are available:

1. Displacement, in which a small quantity of the mixture to be separated is introduced at the top of the column. The introduced sample will be displaced by a liquid or vapor as a displacer which has a higher affinity for the column packing than any of the components of the sample mixtures moves down the column. The components from the

sample mixture will be forced out of the column in the order of their increasing affinity for the column packing. One of the main disadvantages of this method is that the column will retain the displacer.

2. Frontal analysis, in which the sample mixture serves as its own displacer. The sample mixture is forced down and its components will be pushed out of the column by injecting more sample. The first component will be the one which has the lowest affinity for the column packing. In this method, only the first component will be in a pure form.
3. Elution analysis. This is usually the preferred method of development in gas chromatography, in which the sample mixture is introduced into a continuous stream of carrier gas which moves at a rate depending on its partition coefficient K . K is defined as the weight of solute (sample) per milliliter of liquid phase divided by the weight of solute per milliliter of carrier gas. Under favorable conditions, the individual components will have different partition coefficients and will be completely separated. This method has the advantages of regeneration of the column and complete separation of sample components within a short time.

The gas chromatograph consists of a sample injector, the column and the detector, among other parts. A sample injector is a device for introducing a gas or liquid sample into

the gas chromatograph instrument. The column is the part of the apparatus which accomplishes the separation of the sample components. It contains a liquid phase which is essentially non-volatile at the operating temperature of the column. An appropriate liquid coated onto a solid support constitutes the packing for a gas liquid chromatographic column. The sample components are dissolved in this liquid as the sample moves through the column, and the separation of the components depends on their differences in volatility in the solution. Very fine pure solid particles, usually inert, such as diatomaceous earth usually form a solid support for this liquid phase since the greater the surface area, the greater the efficiency of the column. The detector measures the change in composition of the effluent. It measures the amount of sample component in the carrier gas as it leaves the column and enters the detector. A differential detector measures the instantaneous concentration, and the integral detector measures the accumulation of the sample components. The differential detector gives a direct measurement of the peak area. The principle of these detectors is based on thermal conductivity; heat is conducted away from a hot body, situated in a gas, at a rate depending on the nature of the gas, assuming the other factors are constant. The hot body is a wire or wires of some metal which has a high resistance coefficient at high temperatures mounted axially in a space containing the gas. The wire is heated by a constant electric

current. The conductivity of the surrounding gas is a factor determining the temperature of the wire and also its resistance. The latter property is measured. The presence of a foreign substance in the gas is detected on the basis that it has a different thermal conductivity than the carrier gas. A differential procedure to measure thermal conductivity is followed. This is done by employing two gas channels and wires that are, as nearly as possible, identical. Pure carrier gas flows through the first channel, and the same current of gas which has passed through the column flows through the second (23). Any differences in resistance of the two wires due to the effects of the volatile components in the effluent are thus recorded.

Another kind of chromatograph was used in this investigation. It is called a flame ionization detector. It was discussed in Chapter III.

Mass Spectrometer

The chart obtained from the mass spectrometer is called a mass spectrum.

Definition of the Mass Spectrum

The mass spectrum is a pattern of ion beam intensity versus mass/charge for a certain sample. The mass spectrometer ionizes gas molecules at a low pressure and sorts them or their fragments according to their masses.

Objective of the Mass Spectrometer

The purpose of the mass spectrometer is to convert the sample into a product that can be measured and is indicative of the original molecules. The reagent which is initiating the conversion reaction is a beam of energetic electrons. The products formed are gases of positive ions, whose identities and relative abundance are displayed in the mass spectrum. Then the aim is to relate the positive ions formed by the electron bombardment, which are indicated by the mass spectrum, to the molecular structure of the sample.

Parts of the Mass Spectrometer

The most important part in the mass spectrometer is the ion source, which has a pressure without any sample of roughly 10^{-7} Torr to 10^{-10} atm. The bombarding electrons are boiled off an incandescent filament and travel through the ion chamber to an anode on the opposite side. The vaporized sample molecules interact with the beam of electrons to form a variety of products, including positive ions. These positive ions are pushed out (drawn down) of the source by a small repeller potential and then accelerated by a large potential difference between the two electrodes.

Small potentials can be applied to the repeller and to the ion focus plate to produce a definite beam of positive ions in a way analogous to the focusing of a light beam in a spectrophotometer. The bulk of the sample molecules and all

other electrons impacted are removed continuously by a vacuum pump from the ion source.

Theoretical Background of the Mass Spectrometer

Mass spectrometry denotes the analytical field which requires the relative intensity spectrum of charged molecules and their fragments to be ordered according to their mass numbers. The ions produced from the sample by the electron bombardment are accelerated to form a total beam. The beam is deflected in a magnetic field and dispersed into a number of beams, the number of beams depending on the mass charge ratios of the ions. The mass spectrometer presents a trace spectrum with values on a chart by mass scanning.

The sample molecules are introduced into the ion source and are ionized by electrons of about 10 to 80 eV (11). These ions are accelerated to between 1,000 and 10,000 eV and then led into a homogeneous magnetic field where they are deflected in a traversing direction (see Figure 38). The radius of the curved trajectory varies with the mass of the ions. The kinetic energy possessed by the flying ions is given by the following formula:

$$\frac{1}{2} Mv^2 = eV$$

where e = electronic charge

V = acceleration voltage

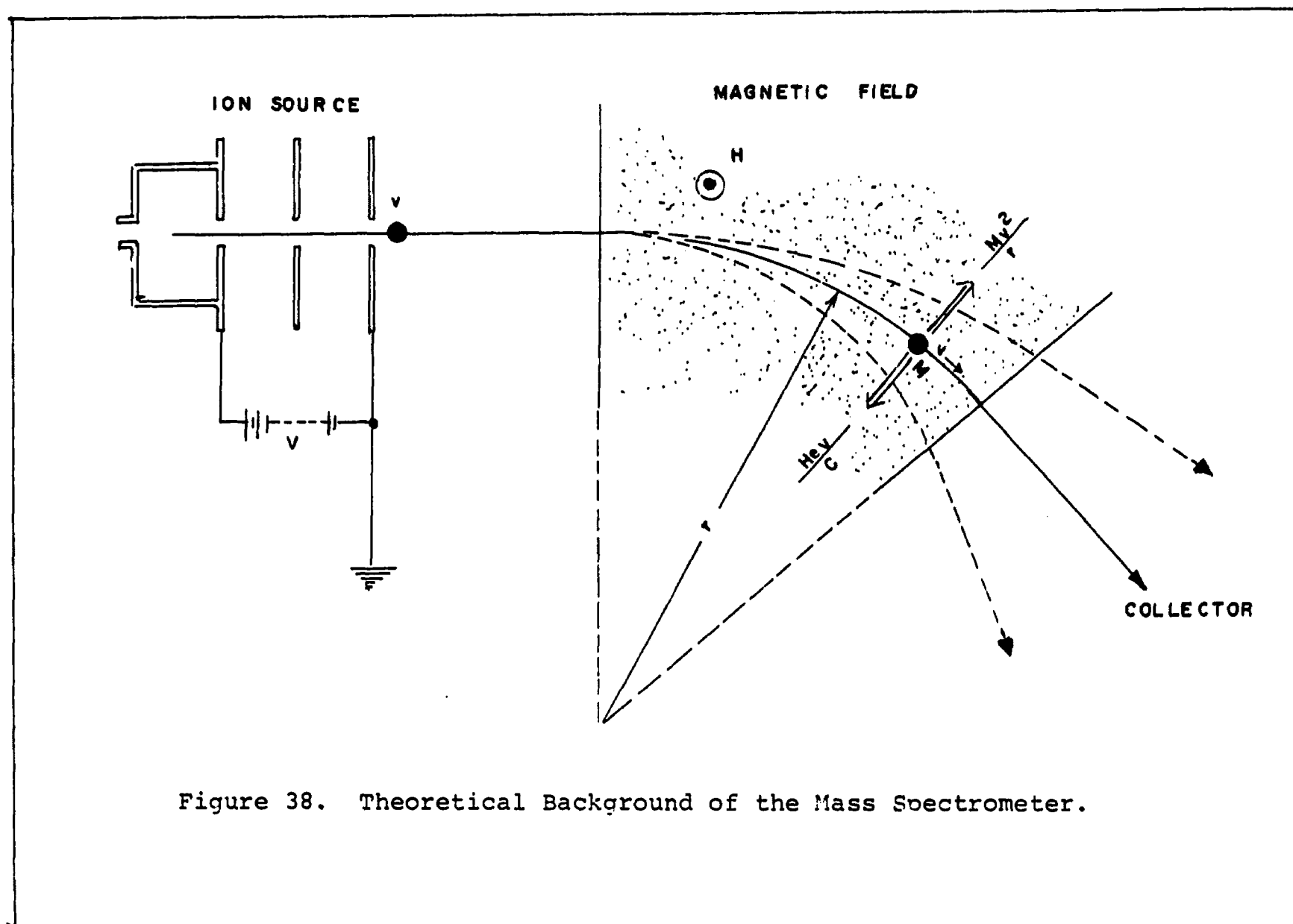


Figure 38. Theoretical Background of the Mass Spectrometer.

M = the mass

v = velocity of the ion

When the ion beam enters perpendicular to the edge of the magnetic field, the ions are subjected to a Lorenz force acting at right angles to both the magnetic field and the flying trajectory direction, and which will be dynamically balanced by the centrifugal force. Hence, the ions will move in a circular path satisfying the following equation:

$$Mv^2/r = Hev/C$$

where C = the velocity of light, 10^{10} cm/sec

H = the intensity of the magnetic field

r = the radius of curvature of the ion trajectory

Combining the two previous equations gives

$$\frac{M}{e} = \frac{r^2 H^2}{2vC^2}$$

or
$$M/e = 4.82 \times 10^{-5} \frac{r^2 H^2}{v}$$

provided M is expressed in mass number, e in charge number, r in centimeters, H in gauss and v in practical volts units. This is the basic formula forming the principle of the single focus mass spectrometer. The mass spectrometer instrument of this type holds r fixed, and either v or H is varied for the purpose of scanning. The mass spectrometer RMU series (11) is of the magnetic scanning type in which the energy is maintained constant throughout the scanning. Figure 39 represents

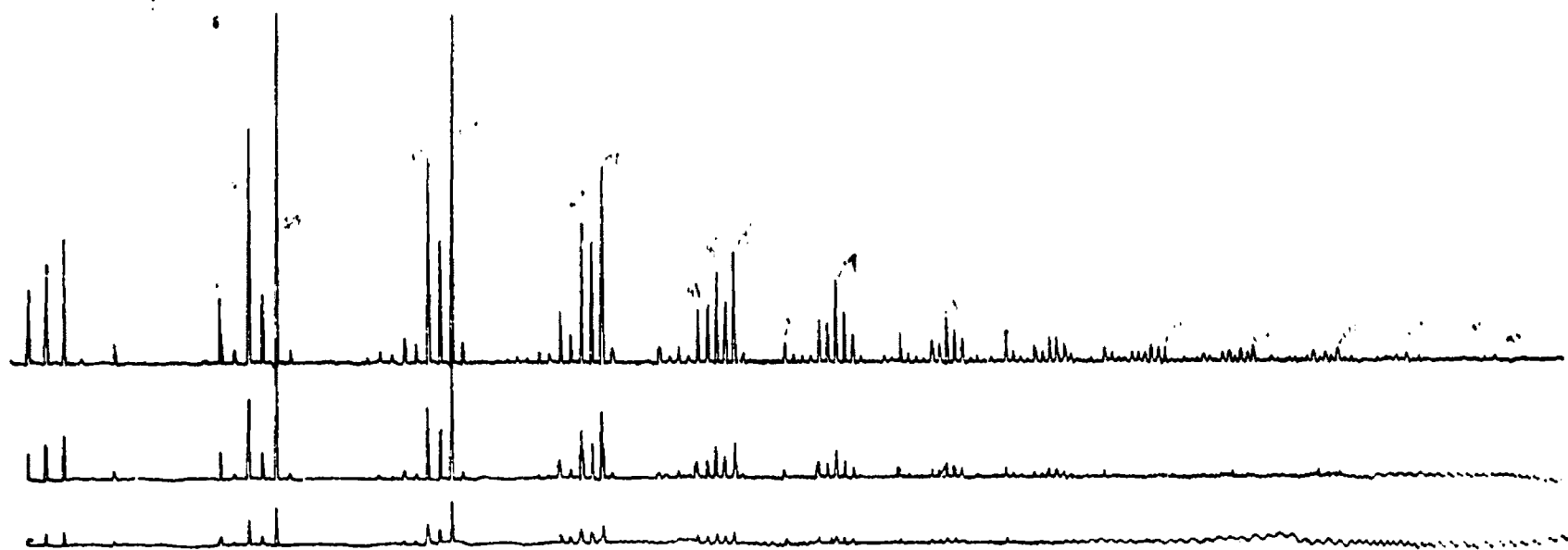


Figure 39. Composite Mass Spectrum of Hydrocarbon Sample C₁A.

a composite chart to illustrate the mass spectrum obtained from RMU series for sample C₁A (condensate obtained from oil API gravity 30.2 at equilibrium pressure of 4500 psig).

APPENDIX B

NOMENCLATURE

C_1A	Condensate obtained after vaporization of oil No. 1 by carbon dioxide at equilibrium pressure A
C_1B	Condensate obtained after vaporization of oil No. 1 by carbon dioxide at equilibrium pressure B
C_1C	Condensate obtained after vaporization of oil No. 1 by carbon dioxide at equilibrium pressure C
C_2A	Condensate obtained after vaporization of oil No. 2 by carbon dioxide at equilibrium pressure A
C_2B	Condensate obtained after vaporization of oil No. 2 by carbon dioxide at equilibrium pressure B
C_2C	Condensate obtained after vaporization of oil No. 2 by carbon dioxide at equilibrium pressure C
C_3A	Condensate obtained after vaporization of oil No. 3 by carbon dioxide at equilibrium pressure A
C_3B	Condensate obtained after vaporization of oil No. 3 by carbon dioxide at equilibrium pressure B
C_3C	Condensate obtained after vaporization of oil No. 3 by carbon dioxide at equilibrium pressure C
C_4A	Condensate obtained after vaporization of oil No. 4 by carbon dioxide at equilibrium pressure A
C_4B	Condensate obtained after vaporization of oil No. 4 by carbon dioxide at equilibrium pressure B
C_4C	Condensate obtained after vaporization of oil No. 4 by carbon dioxide at equilibrium pressure C
R_1A	Residual oil obtained from oil No. 1 at equilibrium pressure A

R_1B	Residual oil obtained from oil No. 1 at equilibrium pressure B
R_1C	Residual oil obtained from oil No. 1 at equilibrium pressure C
R_2A	Residual oil obtained from oil No. 2 at equilibrium pressure A
R_2B	Residual oil obtained from oil No. 2 at equilibrium pressure B
R_2C	Residual oil obtained from oil No. 2 at equilibrium pressure C
R_3A	Residual oil obtained from oil No. 3 at equilibrium pressure A
R_3B	Residual oil obtained from oil No. 3 at equilibrium pressure B
R_3C	Residual oil obtained from oil No. 3 at equilibrium pressure C
R_4A	Residual oil obtained from oil No. 4 at equilibrium pressure A
R_4B	Residual oil obtained from oil No. 4 at equilibrium pressure B
R_4C	Residual oil obtained from oil No. 4 at equilibrium pressure C
O_1	Original oil sample, oil No. 1
O_2	Original oil sample, oil No. 2
O_3	Original oil sample, oil No. 3
O_4	Original oil sample, oil No. 4
1	Denotes a gravity of oil of 30.2 API, measured one year ahead of the experiment time. 29.4 API and 0.8794 gm/cc at 74°F and atmospheric pressure at the time of the experiment
2	Denotes a gravity of oil 24.3 API measured five years ahead of the experiment time. 21.80 API and 0.9230 gm/cc at 74°F and atmospheric pressure at the time of the experiment

- 3 Denotes a gravity of oil 22.7 API measured five years ahead of the experiment time. 21.30 API and 0.9260 gm/cc at 74°F and atmospheric pressure at the time of the experiment
- 4 Denotes a gravity of oil 15.4 API measured five years ahead of the experiment time. 16.9 API and 0.9535 gm/cc at 74°F and atmospheric pressure at the time of the experiment
- A Denotes the equilibrium pressure applied to the four oils during vaporization or condensation at 4500 psig and temperature 74°F
- B Denotes the equilibrium pressure applied to the four oils during vaporization or condensation at 3000 psig and temperature 74°F
- C Denotes equilibrium pressure applied to the four oils during vaporization or condensation at 1500 psig and temperature 74°F
- O Denotes one of the four crude oils. Oil No. 1 received two years ago from water flooded reservoir (Elgin field Thomas lake lease, Sec. 22 T3NR10W). The other three oils received five years ago from water flooded reservoir (Reference 10)
- C Denotes a condensate recovered after vaporization of one of the four oils at one equilibrium pressure and gathered at 32°F and atmospheric pressure
- R Denotes a residual oil remaining from any of the four oils at any of those equilibrium pressures and after recovering the condensate. All residual oils were collected at atmospheric pressure and 74°F
- M Reservoir CO₂ gas cap measured at equilibrium pressure and at 100°F, in cc, divided by the reservoir oil volume at the same conditions; it is a ratio
- m It is M, measured in scf/STB
- B_o Formation volume factor = reservoir oil volume obtained at equilibrium pressure and at 100°F/by the same oil measured at stock tank condition, Res bbl/STB
- GOR Standard cubic feet of gas recovered at standard conditions divided by the volume of the condensate recovered at standard condition, scf/STB

S_{wo}	Gas oil compressibility (oil swelling) or total system compressibility = volume of mercury required to compress the gas and the cell and the mercury inside the cell, from atmospheric pressure to the equilibrium pressure
C_o	Oil compressibility at 1500 psig, cc/cc/psig
CGO	Total cell, gas cap, oil compressibility, cc Hg
GCOR	Gas cap volume to reservoir oil volume ratio. The CO ₂ gas cap produced measured at standard conditions stcuft/reservoir oil volume before carbon dioxide injection and after removing the condensate
M	Gas cap produced in stcuft/stock tank oil volume, stcuft/STB
R_s	Solution gas oil ratio, volume of the gas dissolved divided by the oil volume in which the gas was dissolved (residual oil), stcuft/STB
GC	Gas cap

This is from the computer program in Appendix H and flow chart diagram, Figure 37:

1	= CH ₄
2	= CO ₂
3	= C ₂ H ₆
4	= C ₃ H ₈
5	= C ₄ H ₁₀ ⁺
6	= C ₅ H ₁₂ ⁺
EM	= molecular weight
TC	= critical temperature, °F
AK	= K value = y_i/x_i
X,Y,Z	= their usual meaning as in the program

APPENDIX C

CALCULATION OF B_o AT 1500 PSIG

Oil API gravity	30.2
Equilibrium pressure, psig	1500.00
Equilibrium temperature, °F	100
Volume of the cell measured at standard conditions, cc	660.356
Volume of the oil at standard conditions measured by the mercury pump, cc	275.00 385.356
Volume of mercury required to compress the oil from 14.7 to 1500 psig, cc	5.242 390.598
Volume of liquid carbon dioxide charged and equivalent to cc of mercury withdrawn from the cell	227.661 162.937
Volume of gas cap at equilibrium pressure and at equilibrium temperature, equivalent to cc mercury charged into the cell	167.100
Mercury remains in the cell at equilibrium with the oil	330.037
Reservoir oil volume in the cell, cc	660.356 - 330.037 330.319

$$B_o = \frac{\text{STB}}{\text{Res. bbl}} = \frac{330.319}{264} = 1.250$$

APPENDIX D

CALCULATION OF DATA FED INTO THE PROGRAM OF OIL NO. 1 AT PRESSURE C

Volume of carbon dioxide injected into the cell at
1500 psig, and 34°F = 203.039

Volume of CO₂ produced as vapor at standard condition,
stcuft = 0.7213

Each 0.893 stcuft/45 cc Hg at 1500 psig

$$\frac{0.7213 \times 45}{0.893} = 36.342 \text{ cc Hg equivalent}$$

$$\frac{203.039 \times 0.93}{44.01} = 4.28 \text{ moles CO}_2 \text{ injected}$$

203.039 - 36.3477 = 166.619 cc volume of carbon
dioxide dissolved in the residual oil

$$\frac{36.42 \times 0.93}{44.01} = 0.77 \text{ moles of carbon dioxide produced with the condensate}$$

$$\frac{275 \times 0.8794}{234} = 1.032 \text{ moles of oil fed into the system}$$

4.28 + 1.032 = 5.312 total number of moles

The volumetric loss assumed 5 cc in all the experiments

Moles of condensates produced

$$\frac{11 \times 0.802}{169.2} = 0.0522 \text{ moles}$$

$$11 + 5 = 16 \text{ cc}$$

$$275 - 16 = 259 \text{ cc residual oil}$$

Moles of residual

$$\frac{259 \times 0.8916}{292} = 0.791$$

Material balance equation:

Moles of oil fed into the system = total moles produced

$$0.0522 + 0.791 = 0.8432$$

$$1.032 - 0.8432 = 0.1888 \text{ moles of light ends lost}$$

$$0.1888/5.312 = 0.0352 \text{ ratio of the loss}$$

$$4.28/5.312 = 0.807 \text{ ratio of carbon dioxide fed into the system}$$

$$1.000 - 0.807 = 0.193 \text{ moles residual oil}$$

Moles of

$$C_1H_4 + C_2H_6 + C_3H_8 = 0.0354$$

Moles of C_4H_{10} as obtained from the chromatograph and presented in Table 5 + all the heavy components
= 0.1576 moles

The other equilibrium pressures of this oil 3000 and 4500 and other oil No. 3 for pressure 1500, 3000, and 4500 were calculated exactly in the same manner. Their results are presented in Table 27. The percentage was calculated on the assumption that 167.1 cc in all the experiments of carbon dioxide gas cap was injected in order to have constant evaporation factor. The results are presented in Table 25.

APPENDIX E

CALCULATION OF THE K VALUES OF CO₂ AT PRESSURE 4500 PSIG AND TEMPERATURE 100°F

Volume of liquid CO₂ injected into the cell at 1500 psig,
34°F, cc = 224.106

Moles of CO₂ injected into the cell

$$\frac{224.106 \times 0.93}{44.01} = 4.74$$

Moles of oil introduced into the cell

$$\frac{275 \times 0.8794}{234} = 1.032$$

Moles of condensate recovered

$$\frac{32.0 \times 0.850}{229} = 0.1187$$

Gas recovered, cc, equivalent to mercury in the pump

$$\frac{2.0587 \times 45}{0.893} = 103.4 \text{ cc of CO}_2 \text{ at } 34^\circ\text{F and } 1500 \text{ psig}$$

$$\frac{103.4 \times 0.93}{44.01} = 2.182 \text{ moles of CO}_2 \text{ recovered}$$

$$Y_{\text{CO}_2} = \frac{\text{Moles of CO}_2 \text{ in the vapor phase}}{\text{Total no. of moles of the vapor phase}}$$

$$= \frac{2.182}{2.182 + 0.1187} = 0.948$$

$$4.74 - 2.182 = 2.558 \text{ moles of the CO}_2 \text{ in the liquid}$$

$$1.032 - 0.1187 = 0.9133 \text{ mole of oil}$$

$$X_{\text{CO}_2} = \frac{\text{Moles of CO}_2 \text{ in the liquid phase}}{\text{Total no. of moles of the liquid phase}}$$

$$= \frac{2.558}{0.9133 + 2.5580} = 0.737$$

$$K_i = \frac{Y_i}{X_i} \frac{0.948}{0.738} = 1.289$$

(See Table 28)

APPENDIX F

INTERPRETATION OF SOME OF THE EXPERIMENTAL RESULTS

Oil API gravity	30.2
Volume of oil injected at standard condition, cc	275
Equilibrium temperature, °F	100
Equilibrium pressure, psig	1500
Volume of the cell at STC, cc	660.356
Volume of mercury withdrawn from the cell and equivalent to the volume of oil injected, cc	<u>275.00</u> 385.356
Volume of mercury required to compress the oil from zero psig to the equilibrium pressure 1500 psig, cc	<u>5.242</u> 390.598
Volume of the CO ₂ injected at 1500 psig and 34°F, equivalent to cc mercury withdrawn from the cell, cc	<u>227.661</u> 162.937
Volume of the gas cap (vapor phase) pro- duced at equilibrium pressure, 100°F and equivalent to cc of mercury injected	<u>167.100</u> 330.037

Reservoir oil volume after injection CO ₂ and after production of the vapor phase, cc	660.356
	- 330.037
	<u>330.319</u>

Oil volume before CO ₂ injection at equilibrium pressure, cc	275.000
	- 5.242
	<u>269.758</u>

Reservoir oil volume before CO ₂ injection and at equilibrium pressure but after the condensate was produced	269.758
	- 11.000
	<u>258.758</u>

$$M = \frac{\text{Volume of reservoir vapor phase (gas cap)}}{\text{Volume of reservoir oil volume}}$$

$$= \frac{167.1}{330.319} = 0.506$$

$$B_o = \frac{330.319}{264} = 1.250 \text{ Reser. bbl/STBBL}$$

$$\text{GOR} = \frac{\text{Volume of the gas produced at STC, cuft}}{\text{Volume of the condensate produced at STC}}$$

$$= \frac{0.7213 \text{ cuft}}{11.00 \text{ cc}}$$

$$= \frac{11}{159000} = 6.92 \times 10^{-5} \text{ STBBL condensate}$$

$$\text{GOR} = \frac{0.7213}{6.92 \times 10^{-5}} = 10,400 \text{ stcuft/STB}$$

S_{wo} calculation

Original volume of CO ₂ injected at the equilibrium pressure, 1500 psig, cc	227.661
---	---------

Volume of the vapor phase produced at equilibrium pressure and 100°F, cc	<u>167.100</u>
---	----------------

This CO ₂ left in the oil, in the cell, cc	60.561
---	--------

Reservoir oil volume at equilibrium pressure
and 100°F after the gas was injected, and
the vapor phase was produced, cc 330.319

Reservoir oil volume before the gas injection
but after the condensate production at
equilibrium pressure and 100°F, cc 258.758
71.561

$$S_{wo} = \left| \frac{71.561 - 60.561}{258.758} \right| = 4.25 \text{ percent}$$

C_o calculation

cc/cc/psig at 1500 psig neglecting the
pump steel expansion at that pressure

$$\frac{5.242}{275} = 1.9 \times 10^{-2} \text{ cc/cc/1500 psig}$$

$$\frac{1.9 \times 10^{-2}}{1500} = 12.7 \times 10^{-6} \text{ cc/cc/psig}$$

GCOR calculation

$$\frac{167.1 \times 0.893}{45} = 3.32 \text{ STC ft of vapor}$$

phase produced at equilibrium pressure and 100°F

$$\frac{258.758}{159000} = 1.628 \times 10^{-3} \text{ BBL}$$

$$\frac{3.308}{1.628 \times 10^{-3}} = 2030 \text{ stcuft/Res. BBL}$$

m calculation

$$\frac{3.32 \times 159000}{330.319} = 1600 \text{ scft/Res. BBL}$$

R_s calculation

Volume of the CO_2 injected, cc 227.661

Volume of the gas cap produced, cc 167.1
60.561

Volume of the residual oil at STC, STBBL

$$275 - 11 = 264$$

$$\frac{264}{1.59 \times 10^5} = 1.648 \times 10^{-3} \text{ STB}$$

$$\frac{60.561 \times 0.893}{45} = 1.22 \text{ stcuft}$$

$$R_s = \frac{1.22}{1.648 \times 10^{-3}} = 728 \text{ stcuft/STB}$$

$$\text{CGO} = 5.242$$

APPENDIX G

MOLECULAR WEIGHT CALCULATION

Molecular weight was measured by the standard freezing point depression method. This was based on the fact that in an ideal solution, the forces between molecules are not altered when molecules of more than one kind are mixed. Rault's law applies that the freezing point depression is directly proportional to the molal concentration of the solution. The temperature at which the crystals of the solution first appear and are in equilibrium with the solution is called the freezing point of the solution. Since the freezing point of pure benzene is known, then the difference between the two readings is due to the addition of the hydrocarbon sample, which decreases the tendency of molecules of benzene to escape into the gas, in other words, the solute molecules decrease the vapor pressure of benzene. Each solvent exhibits a specific value for the change in temperature per mole of solute per kilogram of solvent. Then the freezing point depression is nearly proportional to the number of solute molecules in the solution.

$$\Delta T_f = k_f * m$$

where ΔT_f = the experimental freezing point depression

m = the molality of the solution, number of moles of solute in one kilogram of solvent

k_f = molal freezing point depression; for benzene
 $k_f = 5.12$

The above equation was modified

$$m = \frac{W_{su} \times 1000}{W_{sv}}$$

$$M_{su} = \frac{W_{su} \times 1000 \times k_f}{W_{sv} \times \Delta T_f}$$

where M_{su} = molecular weight of the solute, gram mole

W_{sv} = weight of solvent, grams

W_{su} = weight of solute, grams

APPENDIX H

COMPUTER PROGRAM

```

1  N= TOTAL NC. CF MLES
2  Z(1)=MLE FRACTICN CF CCMPNENT 1
3  Y(1)=MLE FRACTICN CF CCMPNENT 1 IN THE VAPOR
4  X(1)=MOLE FRACTICN CF CCMPNENT 1 IN THE LIQUID
5  V= TOTAL NC. CF MLES CF THE VAPOR
6  L= TOTAL NC. CF MLE CF THE LIQUID
7  L= TOTAL NC. CF MLE CF THE LIQUID
8  DIMENSION AK(6),Z(6),Y(6),X(6),EM(6),TC(6)
9  T=100.
10 CC 207 JJ=1.3
11 CC 205 KK=1.6
12 READ (5,13) N
13 FCNMT(15)
14 READ(5,12)(Z(1),I=1,N)
15 READ(5,12)(AK(1),I=1,N)
16 FCNMT(3F10.7)
17 READ(5,100)PCCNV
18 READ(5,100)PMCRK
19 READ(5,100)GRAV
20 READ(5,99)(EW(1),I=1,N)
21 READ(5,99)(TC(1),I=1,N)
22 READ(5,136) WT,TWCL
23 FCNMT(2F10.3)
24 FCNMT(6F10.3)
25 FCNMT(F10.3)
26 ARITE(6,101)PCCNV
27 FCNMT(//.3X,'THE CONVERGENCE PRESSURE =',F15.3)
28 WRITE(6,102)EACHK
29 FCNMT(5X,'THE SYSTEM WORKING PRESSURE =',F15.3)
30 WRITE(6,103)T
31 FCNMT(5X,'THE SYSTEM WORKING TEMPERATURE =',F10.3)

```

```

23      WRITE(6,104)GMAY
24      WRITE(6,107)WT,TMCL
27      FORMAT(5X,'THE MOLECULAR WEIGHT IS ',F10.3,'TMOLES FED INTO THE
      1SYSTEM =',F10.3)
35      FORMAT(5X,'THE OIL API GRAVITY=',F10.3)
29      WRITE(6,105)(I,EN(I),I,TC(I),I=1,N)
30      FORMAT(5X,EN(' ',11.0))=, F20.3,5X,TC(' ',11.0))=,F20.3)
31      WRITE(6,70) N
32      FORMAT(/,5X,'NO. OF COMPONENTS IS N = ',I5)
33      WRITE(6,69)(I,Z(I),I,AK(I),I=1,N)
34      FORMAT(5X,Z(' ',11.0))=,E20.9,5X,AK(' ',11.0))=,E20.9)
35      VC=0.5
36      WRITE(6,90) VO
37      FORMAT(/,5X,'THIS IS THE VALUE OF VO=',E20.9)
38      SUMN=0.0
39      SUMD=0.0
40      DO 14 I=1,N
41      SUMN=SUMN+Z(I)*(AK(I)-1.0)/(VO*(AK(I)-1.0)+1.0)
42      SUMD=SUMD+Z(I)*(AK(I)-1.0)**2/((VO*(AK(I)-1.0)+1.0)**2)
43      CONTINUE
44      VN=VC+SUMN/SUMD
45      DEL=ABS(VN-VC)
46      IF (DEL-.0001) 19,19,16
47      VC=VN
48      GO TO 115
49      V=VN
50      EL=1.0-V
51      ZICNA=C.0
52      GAMMA=C.0
53      DO 24 I=1,N
54      X(I)=Z(I)/((AK(I)-1.0)+V+1.0)
55      Y(I)=X(I)+AK(I)

```

```

56      ZIGMA =ZIGMA+X(I)
57      GAMA=GAMA+Y(I)
58      24  CONTINUE
59      WRITE(6,55)(I,X(I),I,Y(I),I=1,N)
60      55  FORMAT(5X,'X(',I1,')=',E20.9,5X,'Y(',I1,')=',E20.9)
61      WRITE(6,82) ZIGMA,GAMA
62      82  FORMAT(//,5X,'ZIGMA IS THE SUM OF X(I)=',E20.9,5X,
1'GAMA IS THE SUM OF THE Y(I)=',E20.9)
63      WRITE (6,59)V
64      59  FORMAT(5X,'THE NO. OF MOLES OF THE VAPOR IS=V=',E20.9)
65      WRITE(6,60) EL
66      60  FORMAT(//,5X,'THIS IS THE NO. OF MOLES OF THE LIQUID=',E20.9)
67      DO 204 I=1,N
68      X(I)=X(I)*TMCL
69      Y(I)=Y(I)*TMCL.
70      204  CONTINUE
71      WRITE(6,53)(I,X(I),I,Y(I),I=1,N)
72      EL=EL+TMCL*WT
73      WRITE(6,57)EL
74      57  FORMAT(5X,'THE RECOVERY IN CUBIC CC=',F10.3)
75      SSLMN=0.0
76      SSLMD=0.0
77      DO 10 I=2,N
78      SSLMN=SSLMN+X(I)*EM(I)*TC(I)
79      SSLMD=SSLMD+X(I)*EM(I)
80      10  CONTINUE
81      TCF=SSLMN/SSLMD
82      WRITE(6,106)TCF
83      106  FORMAT(5X,'THIS IS THE S CRITICAL TEMPERATURE OF THE SYSTEM EXCLL
1METHANE=',F10.2)
84      205  CONTINUE
85      207  CONTINUE
86      STOP
87      END

```

ELXFC

THE CONVERGENCE PRESSURE = 10000.000
 THE SYSTEM WORKING PRESSURE = 4500.000
 THE SYSTEM WORKING TEMPERATURE = 100.000
 THE CIL API GRAVITY = 30.200
 THE MOLECULAR WEIGHT IS = 355.000 TMOLES FED = 5.774
 EM(1) = 16.040 TC(1) = -115.700
 EM(2) = 44.010 TC(2) = 27.500
 EM(3) = 30.060 TC(3) = 89.770
 EM(4) = 44.090 TC(4) = 205.950
 EM(5) = 58.120 TC(5) = 305.130
 EM(6) = 72.146 TC(6) = 385.600

NO. OF COMPONENTS IS N = 6
 Z(1) = 0.399999900E-01 AK(1) = 0.155000000E 01
 Z(2) = 0.819999900E 00 AK(2) = 0.131499900E 01
 Z(3) = 0.100000000E-01 AK(3) = 0.850000000E 00
 Z(4) = 0.340000000E-02 AK(4) = 0.600000000E 00
 Z(5) = 0.267999900E-02 AK(5) = 0.459999900E 00
 Z(6) = 0.123920000E 00 AK(6) = 0.319999900E 00

THIS IS THE VALUE OF VC = 0.500000000E 00
 X(1) = 0.269394600E-01 Y(1) = 0.41754620E-01
 X(2) = 0.641780700E 00 Y(2) = 0.84394140E 00
 X(3) = 0.115238600E-01 Y(3) = 0.97952850E-02
 X(4) = 0.525201100E-02 Y(4) = 0.31512060E-02
 X(5) = 0.511492700E-02 Y(5) = 0.23528940E-02
 X(6) = 0.309390000E 00 Y(6) = 0.99004800E-01

GAMA IS THE SUM OF THE Y(I) = 0.100000000E 01

ZIGMA IS THE SUM OF X(I) = 0.100000000E 01

THE NO. OF MOLES OF THE VAPOR IS = V = 0.881573400E 00

THIS IS THE NO. OF MOLES OF THE LIQUID = 0.112426500E 00
 X(1) = 0.153542600E 00 Y(1) = 0.24109110E 00
 X(2) = 0.370564100E 01 Y(2) = 0.48729170E 01
 X(3) = 0.665388100E-01 Y(3) = 0.56557970E-01
 X(4) = 0.303251100E-01 Y(4) = 0.18195060E-01
 X(5) = 0.295339300E-01 Y(5) = 0.13585600E-01
 X(6) = 0.178641700E 01 Y(6) = 0.57165370E 00

THE RESIDUAL IN CUBIC CC = 242.747

THIS IS THE S CRITICAL TEMPERATURE OF THE SYSTEM EXCLD

METHANE = 218.88

THE RECOVERY (CONDENSATE) = 32.253 CC

THE CONVERGENCE PRESSURE = 10000.000
 THE SYSTEM WORKING PRESSURE = 3000.000
 THE SYSTEM WORKING TEMPERATURE = 100.000
 THE OIL API GRAVITY = 30.200
 THE MOLECULAR WEIGHT IS = 303.000
 MOLES FED = 7.091
 EN(1) = 16.040 TC(1) = -116.700
 EN(2) = 44.010 TC(2) = 87.500
 EN(3) = 30.060 TC(3) = 89.770
 EN(4) = 44.090 TC(4) = 205.950
 EN(5) = 58.120 TC(5) = 305.130

NO. OF COMPONENTS IS N = 5
 Z(1) = 0.999999900E-03 AK(1) = 0.194999900E C1
 Z(2) = 0.855000000E 00 AK(2) = 0.131499900E C1
 Z(3) = 0.190000000E-01 AK(3) = 0.800000000E C0
 Z(4) = 0.499999800E-02 AK(4) = 0.500000000E C0
 Z(5) = 0.120000000E 00 AK(5) = 0.325999900E C0

THIS IS THE VALUE OF VC = 0.500000000E 00
 X(1) = 0.542132400E-03 Y(1) = 0.10571570E-02
 X(2) = 0.667947900E 00 Y(2) = 0.87835120E 00
 X(3) = 0.231088300E-01 Y(3) = 0.18487060E-01
 X(4) = 0.900105300E-02 Y(4) = 0.45005260E-02
 X(5) = 0.299400400E 00 Y(5) = 0.97604510E-01

GAMMA IS THE SUM OF THE Y(I) = 0.100000000E 01
 ZIGMA IS THE SUM OF X(I) = 0.100000000E 01
 THE NO. OF MOLES OF THE VAPOR IS = V = 0.889019300E 00

THIS IS THE NO. OF MOLES OF THE LIQUID = 0.110980600E C0
 X(1) = 0.384426000E-02 Y(1) = 0.74963040E-02
 X(2) = 0.473641700E 01 Y(2) = 0.62283870E 01
 X(3) = 0.163864700E 00 Y(3) = 0.13109170E C0
 X(4) = 0.638264400E-01 Y(4) = 0.31913230E-01
 X(5) = 0.212304700E 01 Y(5) = 0.69211350E 00
 THE RESIDUAL IN CUBIC CC = 232.450
 THIS IS THE CRITICAL TEMPERATURE OF THE SYSTEM EXCLU
 METHANE = 167.84

THE RECOVERY (CONDENSATE) = 36.55 CC

THE CONVERGENCE PRESSURE = 10000.000
 THE SYSTEM WORKING PRESSURE = 1500.000
 THE SYSTEM WORKING TEMPERATURE = 100.000
 THE CIL API GRAVITY = 30.200
 THE MOLECULAR WEIGHT IS = 292.000 MOLES FED = 5.311
 EM(1) = 16.040 TC(1) = -116.700
 EM(2) = 44.010 TC(2) = 87.900
 EM(3) = 30.060 TC(3) = 89.770
 EM(4) = 44.090 TC(4) = 205.950
 EM(5) = 58.120 TC(5) = 305.120

NO. OF COMPONENTS IS N = 5
 Z(1) = 0.300000000E-01 AK(1) = 0.300000000E C1
 Z(2) = 0.806999900E 00 AK(2) = 0.175000000E C1
 Z(3) = 0.100000000E-01 AK(3) = 0.800000000E C0
 Z(4) = 0.539999800E-02 AK(4) = 0.399999900E C0
 Z(5) = 0.157599900E 00 AK(5) = 0.191999900E C0

THIS IS THE VALUE OF VC = 0.500000000E C0
 X(1) = 0.112773800E-01 Y(1) = 0.33832160E-01
 X(2) = 0.497358700E 00 Y(2) = 0.87037780E C0
 X(3) = 0.119906800E-01 Y(3) = 0.95925440E-02
 X(4) = 0.107581200E-01 Y(4) = 0.43032720E-02
 X(5) = 0.478615000E 00 Y(5) = 0.91894030E-01

GAMA IS THE SUM OF THE Y(I) = 0.100999900E 01
 ZIGMA IS THE SUM OF X(I) = 0.100999900E 01
 THE NO. OF MOLES OF THE VAPOR IS = V = 0.230094900E C0

THIS IS THE NO. OF MOLES OF THE LIQUID = 0.169905100E C0
 X(1) = 0.598942000E-01 Y(1) = 0.17968260E C0
 X(2) = 0.264147100E 01 Y(2) = 0.46225760E C1
 X(3) = 0.636824900E-01 Y(3) = 0.50946000E-01
 X(4) = 0.571367200E-01 Y(4) = 0.22854670E-01
 X(5) = 0.254192300E 01 Y(5) = 0.48204910E C0

THE RESIDUAL IN CUBIC CC = 263.491
 THIS IS THE S CRITICAL TEMPERATURE OF THE SYSTEM EXCLU
 METHANE = 208.58

THE RECOVERY (CONDENSATE) = 11.509 CC

THE CONVERGENCE PRESSURE = 10000.000
 THE SYSTEM WORKING PRESSURE = 4500.000
 THE SYSTEM WORKING TEMPERATURE = 100.000
 THE CIL API GRAVITY = 22.700
 THE MOLECULAR WEIGHT IS = 387.000 MOLES FED = 5.260
 EM(1) = 16.040 TC(1) = -116.700
 EM(2) = 44.010 TC(2) = 87.900
 EM(3) = 30.060 TC(3) = 89.770
 EM(4) = 44.090 TC(4) = 205.950
 EM(5) = 58.120 TC(5) = 305.130
 EM(6) = 72.146 TC(6) = 385.600

NO. OF COMPONENTS IS N = 6
 Z(1) = 0.399999900E-01 AK(1) = 0.155000000E C1
 Z(2) = 0.805000000E 00 AK(2) = 0.136999900E C1
 Z(3) = 0.100000000E-01 AK(3) = 0.850000000E C0
 Z(4) = 0.279999900E-02 AK(4) = 0.600000000E C0
 Z(5) = 0.209999900E-02 AK(5) = 0.459999900E C0
 Z(6) = 0.140100000E 00 AK(6) = 0.319999900E C0

THIS IS THE VALUE OF VC = 0.500000000E C0
 X(1) = 0.270251700E-01 Y(1) = 0.41899010E-C1
 X(2) = 0.608476100E 00 Y(2) = 0.83361210E C0
 X(3) = 0.115066400E-01 Y(3) = 0.97806450E-02
 X(4) = 0.430216200E-02 Y(4) = 0.25812970E-02
 X(5) = 0.397254300E-02 Y(5) = 0.18273720E-02
 X(6) = 0.344717500E 00 Y(6) = 0.11030950E C0

GAMA IS THE SUM OF THE Y(I) = 0.999999900E 00

ZIGMA IS THE SUM OF X(I) = 0.100000000E 01

THE NO. OF MOLES OF THE VAPOR IS = V = 0.872912200E C0

THIS IS THE NO. OF MOLES OF THE LIQUID = 0.127087700E C0
 X(1) = 0.142152300E 00 Y(1) = 0.22033610E C0
 X(2) = 0.320658400E 01 Y(2) = 0.43847990E 01
 X(3) = 0.605249400E-01 Y(3) = 0.51446190E-01
 X(4) = 0.226293700E-01 Y(4) = 0.13577620E-01
 X(5) = 0.208956000E-01 Y(5) = 0.96119750E-02
 X(6) = 0.181321300E 01 Y(6) = 0.58022820E C0

THE RESIDUAL IN CUBIC CC = 258.702

THIS IS THE CRITICAL TEMPERATURE OF THE SYSTEM EXCLU

METHANE = 230.55

THE RECOVERY (CONDENSATE) = 16.298 CC

THE CONVERGENCE PRESSURE = 10000.000
 THE SYSTEM WORKING PRESSURE = 3000.000
 THE SYSTEM WORKING TEMPERATURE = 100.000
 THE CIL API GRAVITY = 22.700
 THE MOLECULAR WEIGHT IS = 379.000 MCLES FED = 5.400
 EN(1) = 16.040 TC(1) = -116.700
 EN(2) = 44.010 TC(2) = 87.900
 EN(3) = 30.060 TC(3) = 89.770
 EN(4) = 44.030 TC(4) = 205.950
 EN(5) = 58.120 TC(5) = 305.130

NO. OF COMPONENTS IS N = 5
 Z(1) = 0.390000000E-01 AK(1) = 0.194999900E C1
 Z(2) = 0.810000000E 00 AK(2) = 0.136999900E C1
 Z(3) = 0.999999900E-03 AK(3) = 0.800000000E C0
 Z(4) = 0.240000000E-02 AK(4) = 0.500000000E C0
 Z(5) = 0.147599900E 00 AK(5) = 0.323000000E C0

THIS IS THE VALUE OF VC = 0.500000000E C0
 X(1) = 0.213171700E-01 Y(1) = 0.41568480E-01
 X(2) = 0.612211300E 00 Y(2) = 0.83672940E 00
 X(3) = 0.121158300E-02 Y(3) = 0.96926650E-03
 X(4) = 0.425973500E-02 Y(4) = 0.21258670E-02
 X(5) = 0.361000300E 00 Y(5) = 0.11660300E 00

GAMA IS THE SUM OF THE Y(I) = 0.100000000E 01
 ZIGMA IS THE SUM OF X(I) = 0.100000000E 01
 THE NO. OF MCLES OF THE VAPOR IS = V = 0.871170100E 00

THIS IS THE NO. OF MCLES OF THE LIQUID = 0.126829800E C0
 X(1) = 0.115112700E 00 Y(1) = 0.22446970E C0
 X(2) = 0.330594000E 01 Y(2) = 0.45291380E C1
 X(3) = 0.654254800E-02 Y(3) = 0.52340360E-02
 X(4) = 0.230025600E-01 Y(4) = 0.11501280E-01
 X(5) = 0.194940000E 01 Y(5) = 0.62965650E C0

THE RESIDUAL IN CLRIC CC = 259.570
 THIS IS THE S CRITICAL TEPERATURE OF THE SYSTEM EXCLU
 METHANE = 183.02

THE RECOVERY (CONDENSATE) = 15.436 CC
 THE CONVERGENCE PRESSURE = 10000.000
 THE SYSTEM WORKING PRESSURE = 1500.000
 THE SYSTEM WORKING TEMPERATURE = 100.000
 THE CIL API GRAVITY = 22.700

THE MOLECULAR WEIGHT IS = 375.0001 MOLES FED = 5.080

CA(1)=	16.040	TC(1)=	-116.700
CA(2)=	44.010	TC(2)=	87.500
CA(3)=	30.060	TC(3)=	89.770
CA(4)=	44.090	TC(4)=	205.950
CA(5)=	59.120	TC(5)=	305.130

NO. OF COMPONENTS IS N = 5

Z(1)=	0.999999900E-03	AK(1)=	0.300000000E 01
Z(2)=	0.796999900E 00	AK(2)=	0.175000000E 01
Z(3)=	0.690000000E-01	AK(3)=	0.800000000E 00
Z(4)=	0.200000000E-02	AK(4)=	0.399999900E 00
Z(5)=	0.130930000E 00	AK(5)=	0.193000000E 00

THIS IS THE VALUE OF VL= 0.500000000E 00

X(1)=	0.367735500E-03	Y(1)=	0.11032060E-02
X(2)=	0.484571000E 00	Y(2)=	0.84799930E 00
X(3)=	0.833266900E-01	Y(3)=	0.66661350E-01
X(4)=	0.413054900E-02	Y(4)=	0.16522190E-02
X(5)=	0.427534000E 00	Y(5)=	0.92514040E-01

GAMA IS THE SUM OF THE Y(I)= 0.999930100E 00

ZIGMA IS THE SUM OF X(I)= 0.999930000E 00

THE NO. OF MOLES OF THE VAPOR IS=V= 0.859672100E 00

THIS IS THE NO. OF MOLES OF THE LIQUID= 0.140327800E 00

X(1)=	0.126809600E-02	Y(1)=	0.56042850E-02
X(2)=	0.246162000E 01	Y(2)=	0.43078360E 01
X(3)=	0.423299600E 00	Y(3)=	0.33863500E 00

X(4)=	0.209521800E-01	Y(4)=	0.83932720E-02
X(5)=	0.217187200E 01	Y(5)=	0.41917130E 00

THE RECOVERY IN CUBIC CC= 267.324

THIS IS THE S CRITICAL TEMPERATURE OF THE SYSTEM EXCLU

METHANE= 198.91

THE RECOVERY (CONDENSATE) = 7.676 CC

THE CONVERGENCE PRESSURE = 5000.000

THE SYSTEM WORKING PRESSURE= 4500.000

THE SYSTEM WORKING TEMPERATURE = 100.000

THE LIQUID GRAVITY= 30.200

THE MOLECULAR WEIGHT IS = 355.0001 MOLES FED = 5.774

CA(1)=	16.040	TC(1)=	-116.700
CA(2)=	44.010	TC(2)=	87.500

PM(1)=	30.060	TC(1)=	83.770
PM(4)=	44.070	TC(4)=	205.950
PM(5)=	59.120	TC(5)=	305.130
PM(6)=	72.146	TC(6)=	385.600

NO. OF COMPONENTS IS N = 6

Z(1)=	0.339999900E-01	AK(1)=	0.119999900E C1
Z(2)=	0.219999900E 00	AK(2)=	0.128299900E C1
Z(3)=	0.100000000E-01	AK(3)=	0.100000000E C1
Z(4)=	0.340000000E-02	AK(4)=	0.850000000E C1
Z(5)=	0.267999900E-02	AK(5)=	0.900000000E C0
Z(6)=	0.123920000E 00	AK(6)=	0.900000000E C0

THIS IS THE VALUE OF VC= 0.500000000E C0

X(1)=	0.225040500E-01	Y(1)=	0.27004860E-C1
X(2)=	0.390456900E 00	Y(2)=	0.50095610E C0
X(3)=	0.100000000E-01	Y(3)=	0.10000000E-C1
X(4)=	0.815531200E-02	Y(4)=	0.69320120E-02
X(5)=	0.120427000E-01	Y(5)=	0.96341630E-C2
X(6)=	0.556840400E 00	Y(6)=	0.44547230E C0

GAMA IS THE SUM OF THE Y(I)= 0.999999400E 00

ZIGMA IS THE SUM OF X(I)= 0.999999400E 00

THE NO. OF MOLES OF THE VAPOR IS=V= 0.388729300E C1

THIS IS THE NO. OF MOLES OF THE LIQUID= -0.288729300E C1

X(1)=	0.129932300E 00	Y(1)=	0.15592600E C0
X(2)=	0.225449700E 01	Y(2)=	0.28925200E C1
X(3)=	0.577400100E-01	Y(3)=	0.57740010E-C1
X(4)=	0.470287700E-01	Y(4)=	0.40025430E-01
X(5)=	0.695345400E-01	Y(5)=	0.55627650E-C1
X(6)=	0.321515600E 01	Y(6)=	0.25721560E C1

THE RECOVERY IN CURIC CC= -5912.285

THIS IS THE 5 CRITICAL TEMPERATURE OF THE SYSTEM EXCLL

METHANE= 294.90