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THERMODYNAMIC (PVT) STUDIES OF HYDROCARBONS AND THEIR ROLE IN ASSESSING RESERVOIR POTENTIAL

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CONTENTS

SUMMARY

The recovery efficiency of hydrocarbons from reservoirs is dependent in part on their fluid characteristics. In order to fully comprehend and evaluate these characteristics, a sample of hydrocarbons has to be obtained from the formation and tested at conditions of reservoir temperature and pressure.

Using specially developed apparatus, two distinct laboratory test programs are carried out, one for crude (black) oil samples and one for gas condensates.

A typical crude oil PVT testing program covers the following measurements:

(1) fluid compressibility
(2) fluid saturation pressure
(3) gas/oil ratios
(4) viscosity
(5) fluid density
(6) fluid characteristics under 'differential' and 'flash' liberation processes from reservoir to stock tank
(7) component analysis of gases and liquids

Gas condensates are generally regarded to exist in a gaseous state at reservoir conditions; laboratory tests to evaluate the characteristics of these fluids are therefore designed accordingly with the main consideration being the determination of phase properties at various pressure/temperature conditions.

The equipment used for gas condensate and crude oil analysis is generally interchangeable, although gas condensates do require the use of a special "visual" cell to permit observation and measurement of phase types formed at various temperature/pressure conditions.

Compressibility measurements to determine the deviation of natural gas from the ideal gas laws are sometimes determined, particularly where significant amounts of H_2S and CO_2 are present. Otherwise, deviation may be calculated from molecuear component analysis.

Thermodynamic (PVT) studies of hydrocarbons and their role in assessing reservoir potential

I.   INTRODUCTION

The behaviour of hydrocarbon reservoirs cannot be accurately predicted or fully understood without complete knowledge of the chemical and physical characteristics of the hydrocarbons which these reservoirs contain. At least one representative sample of the reservoir fluid must be obtained, and the fluid properties carefully measured, if any comprehensive plan of controlled reservoir performance is to be inaugurated. These data, in conjunction with sound geological work, core analysis, electric logs, reservoir engineering studies, and other information should be used to establish a plan of production, the object of which is to prolong the life and efficiency of the reservoir, and to achieve maximum return for investment.

II.   DISCUSSION

Hydrocarbons are predominantly compounds of carbon and hydrogen although inorganic components such as carbon dioxide, hydrogen sulphide, helium, and nitrogen may also be present.

There are three classes of compounds, which comprise practically all hydrocarbon reservoir content, namely paraffinic, naphthenic, and aromatic (Kennerly, n.d.). Paraffinic hydrocarbons have a straight or branched chain molecular structure, and their general chemical formula is CnH_{2n+2}. Naphthenic hydrocarbons or cycloparaffins are composed of a (molecular) ring structure; their general formula is CnH_{2n}. Aromatic hydrocarbons or the benzene series are unsaturated and may be easily oxidized; as such, they represent the rarest type of hydrocarbons encountered.

Fluids from oil reservoirs are very complex mixtures of compounds containing widely varying amounts of methane, ethane, and higher molecular weight homologues. Natural gas and condensates are generally composed of the lighter homologues, mainly C_1 to C_7. The following table summarizes the components contained in three types of reservoir fluids.

TABLE 1

Composition of typical reservoir fluids

Component	Dry gas reservoir (Mole %)	Gas condensate reservoir (Mole %)	Condensate from separator (Mole %)	Stock tank crude oil (Mole %)
C_1	96.00	85.00	13.50	22.60
C_2	2.00	5.00	4.90	1.70
C_3	0.60	2.00	5.10	0.80
C_4	0.30	1.50	5.90	0.90
C_5	0.20	0.80	7.00	0.50
C_6	0.10	0.60	7.90	0.60
C_{7+}	0.80	5.10	55.70	72.90
Gravity (°API)	-	-	51	16

Two procedures are available for collecting samples of hydro-carbon liquid-phase reservoir fluids. The liquid may be collected with subsurface sampling equipment (Figure 1) which is lowered into the well on a wire line, or samples of the oil and gas may be collected at the surface and later recombined to the produced gas-oil ratio measured at the time the samples were obtained. Regardless of which method is used, the sample should be obtained before any appreciable decline in reservoir pressure has taken place, and thereafter at frequent intervals throughout the life of the reservoir.

This is to enable analysis to be performed on a sample which represents as closely as possible the true fluid as it exists in the reservoir at discovery and also later during production.

The amount of bottom hole sampling carried out in any particular field may vary considerably, but it is generally desirable to have samples of hydrocarbons from each well drilled (Kennerly, n.d.). Additionally, where multiple separate pay zones are encountered in a well, fluid samples of each hydrocarbon zone should be taken. This is to enable a full and proper evaluation of the field wide reservoir fluid producing characteristics.

A. Sampling

1. Bottomhole sampling

When bottomhole sampling of a reservoir fluid is to be carried out, a static pressure gradient survey is initially conducted in the well to determine the reservoir pressure.

Intermediate stops near the top and bottom of the hydrocarbon-producing zone are made with the pressure bomb in order to determine the presence or absence of gas-oil and water-oil levels. A maximum recording thermometer is run in conjunction with the pressure gauge to measure the reservoir temperature at the sampling point.

If the pressure survey shows that no water exists, the bottom hole sampler is lowered on a wire line through a lubricator on the Christmas tree and down the well bore to the mid-point of the hydrocarbon producing interval. Most samplers are lowered into the well with the valves open so that the well fluid passes through them as they are lowered to bottom. Figure 1 illustrates two types of bottomhole samplers.

When the bomb is at sampling depth, the well is produced for a short period to allow fresh fluid to flow into the well bore and the sampler. The sampler is then closed by 'spudding' the wire line. This actuates a set of jars which in turn shear a pin causing the sampler valves to close and trap the fluid. Clocks may also be used for this same purpose, the valves being automatically closed after a predetermined time.

When the sample bomb is raised to the surface, a procedure is immediately carried out to determine the bubble point or saturation pressure of the fluid at atmospheric temperature; this being conducted by the injection of mercury in incremental steps. After each injection the sampler is agitated and the pressure in the bomb recorded. As long as a gas phase is present in the sampler, relatively small pressure increases will be obtained for each increment of mercury injected; this is because of the high compressibility of the two-phase system. These pressure increases are generally between 5 and 35 psig depending on the nature of the reservoir fluid (Kennerly, n.d.).

As soon as the last of the gas phase has been forced into solution in the liquid by the increasing pressure, an abrupt change in the slope of the mercury volume vs. pressure curve is noted, and the compressibility of the fluid system decreases rapidly. Pressure increases of from 100 to 300 psig are then obtained by the injection of an identical amount of mercury, which previously produced only a small pressure change in the two phase region. The two portions of the pressure-volume curve intersect at the bubble point pressure, although as shown later, this may be somewhat difficult to distinguish with certain types of oils. The bubble point characteristics of a typical bottomhole sample are shown in Figure 2.

It is standard procedure to collect a duplicate sample of the reservoir fluid by making another bottomhole sample run, in order to check the first results. (This second sample is subjected to the same tests as previously). Agreement between the valve opening pressures and the bubble point pressure of the two samples at surface temperatures should be very close; generally the difference should be no more than 25 psig (Kennerly, n.d.).

The practice of running two samplers and obtaining agreement of the opening and bubble point pressure ensures that both samplers were closed at the same depth and that no appreciable change in the fluid present at the sampling point has taken place during sampling operations. All of this checking is conducted at the well site to eliminate the possibility of collecting unrepresentative samples.

After both samplers have been checked and found in agreement, the fluids are transferred from the sampler to a high-pressure shipping container for safe transport and subsequent laboratory testing. The transfer operation using a mercury pump is shown in Figure 3.

2. Recombination samples

In conditioning a well preparatory to collecting surface separator samples for recombination, the same degree of care as previously described for subsurface sampling must be exercised. The well is initially flowed through a constant choke size for a period of about 72 hours, although this may be dependent on reservoir type. During this flow period, three separate gas-oil ratio measurements are made during the last 24 hours; if these ratios do not indicate stabilization in the well, the test period must be extended and additional measurements carried out until stabilization occurs. It is also necessary to ensure that other conditions such as pressure, meter temperature etc are maintained constant.

When satisfactory (stabilized) conditions at the well have been established, samples of separator gas and liquid are obtained and transported to the laboratory for subsequent recombination. The containers are checked for leaks on arrival, and provided none have occurred, the samples are combined to the produced gas-oil ratio. After recombination, a laboratory separator test is made on the recombined mixture at the field sampling temperature and pressure. This laboratory gas-oil ratio should not differ from the field ratio by more than 2.5 percent (Kennerly, n.d.).

B. Laboratory testing

Two distinct procedures are followed in the laboratory testing of reservoir fluids, one for crude oil samples and the other for gas condensate samples. These procedures are shown schematically in Figures 4 and 5. Reservoir crude oil samples are derived from bottomhole or recominbation samples; samples for the study of gas condensates are usually best obtained from the recombination of surface wellhead separator samples.

Crude oil reservoirs

The information obtained from the usual fluid study of a crude oil reservoir sample should include the following properties:

1. Compressibility factor of the saturated reservoir oil (Figure 6)
2. Bubble point pressure of the reservoir oil (Figure 6)
3. Solution and evolved gas-oil ratios and liquid phase volumes
4. Viscosity of the reservoir oil phase present during the various liberation processes as a function of pressure (Figure 7)

5.   Differential liberation of the gas phase from the
            sample at reservoir temperature to provide:

        (a) The shrinkage of the liquid phase as a
              function of pressure (Figure 8)
        (b) Formation volume factors
        (c) Gravity of the residual oil
        (d) Solubility of the gas in the oil as
              a function of pressure (Figure 9)
        (e) Gravity of the liquid phase as a
              function of pressure (Figure 10)
        (f) Compressibility of the liberated gas phase
              as a function of pressure (Figure 11)
        (g) The gravity or density of the liberated gas
              at atmospheric conditions (Figure 12)

6.   Equilibrium ratios
7.   Fractional analysis

1. Compressibility factor

In an undersaturated reservoir (one in which the oil is capable
of holding additional gas in solution at the specified state), compressibility
factors indicate the behaviour of the reservoir fluid under pressure decline
from the pressure at which it exists in the reservoir to the bubble point
pressure. In an undersaturated reservoir which has no water drive, all
fluid production obtained while reservoir pressure is above the bubble point
is due to expansion of the single phase reservoir fluid. Compressibility
factors can in this case be used to estimate oil in place and also the
amount recoverable by natural depletion.

Compressibility measurements are determined in the laboratory
using a liquid phase PVT cell immersed in a controlled temperature oil bath.
The cell is initially charged with the reservoir crude; when the cell and
contents reach the desired temperature, compressibility measurements are
determined by means of a mercury pump from which mercury can be injected or
withdrawn from the charged cell. Pressure measurements are made with a
gauge or pressure transducer and the compressibility values for the sample
calculated from the readings. The apparatus showing a visual type PVT cell
is shown in Figure 14.

2. Bubble point

The bubble point or saturation pressure at any specified
temperature may be defined as that pressure at which gas is first released
from solution (Kennerly, n.d.). The bubble point pressure of a reservoir
fluid is of great significance, since it indicates at what pressure
a free gas saturation will be formed in the pores of the reservoir rock.
Bubble point pressure also indicates the reservoir pressure at which oil
viscosity will begin to increase due to the release of gas from solution.

It is desirable to prevent excessive liberation of gas in the reservoir since the accumulation of free gas in the pores of the formation decreases the permeability to oil and increases the permeability to gas. These alterations in the permeability relationship cause increases in gas-oil ratios and decrease in oil production rates by gas blockage. Reservoir pressure should therefore be maintained about the bubble point pressure if the relevant economics are favourable.

Bubble point pressures are determined in the liquid phase PVT cell as described in the study of fluid compressibility. The method of determining bubble points was described previously in the sampling procedure, and will not be repeated here. However, it should be pointed out that the accuracy of the saturation pressure depends upon the nature of the oil being studied. For example, a heavy oil with a lean solution gas will tend to yield a sharply breaking pressure/volume curve, furnishing an accurate saturation pressure. On the other hand, a high gravity oil with rich solution gas will give a pressure/volume curve, the slope of which does not change abruptly at the saturation pressure, making the bubble point much harder to determine.

However, accurate saturation pressure values of high gravity oils can be attained by substituting a 'visual' cell for the 'blind' PVT cell normally used. This visual cell (shown in Figure 14) is almost identical to the blind cell, except that it contains a thick glass window which allows observation of the cell contents during experimentation. Thus, the interpretation of curves to determine the saturation pressure is greatly improved, since this pressure is characterized by the separation of a minute (visible) bubble of gas from the liquid phase.

3. Solution and evolved gas-oil ratios and liquid phase volumes

Gas is evolved from oil in the reservoir by a process which is probably similar to that known as differential vaporization, although a combination of differential and flash vaporization may occur (Pirson, 1958). Differential liberation of gas simply means that the gas liberated is removed from contact with the remaining liquid as soon as the gas is formed (Kennerly, n.d.). In a flash liberation, the pressure is reduced by a finite amount and after equilibrium is established, gas is bled off, with the pressure remaining equalised.

As gas is liberated from the reservoir oil within the formation, the oil phase shrinks, and gas fills the pore space made available by the oil shrinkage. Differential liberation gives data on the oil phase volume at several values of reservoir pressure between the bubble point and zero psig. It is also possible to calculate the free gas saturation in the pores at each of these pressures (Kennerly, n.d.). The liberated and dissolved gas-oil ratio data determined during the liberation process are used in reservoir engineering calculations in conjunction with relative permeability

and liquid phase volume data to make predictions of the future gas-oil ratio and cumulative oil production at any given reservoir pressure throughout the life of a field.

The measurement of solution gas-oil ratios and the resultant liquid phase volumes is carried out in the liquid phase visual PVT cell as described previously (Figure 14). Using this cell, the flash vaporization process is simulated by the removal of the gas phase at constant pressure from the cell. The location of a visible outlet at the apex of the cell permits the rapid removal of all but a very small fraction of the gas without danger of the equilibrium liquid being lost. Differential vaporization can also be determined by gradually reducing the pressure to below the bubble point, and maintaining a constant volume gas bubble at the apex of the cell, while withdrawing gas from the upper outlet. The resultant shrinkage in oil volume is compensated for and measured by injection of mercury from a pump.

A flash equilibrium separator is also available for use in conjunction with the liquid phase cell, and also for certain tests to determine gas-oil ratios and shrinkage factors. A schematic diagram of this apparatus in shown in Figure 15.

4. Viscosity determinations

Viscosity is defined as the internal resistance to fluid flow (Kennerly, n.d.). Oil viscosity increases below the bubble point pressure due to the liberation of gas from the oil. Oil viscosity data are required for use with gas viscosity, free gas saturation, and gas and oil relative permeability data to compute the proportions of gas and oil flowing through the reservoir at any particular time.

Oil and gas viscosity data are equally as important as differential liberation data in making predictions of the produced gas-oil ratio and cumulative oil production at any time in the life of a reservoir. In the event of secondary recovery operations such as waterflooding, oil viscosity characteristics at reservoir conditions are likewise important, since the oil-water viscosity ratio is a very significant factor in waterflood performance.

Most reservoir fluid laboratory tests involving viscosity measurements are conducted in a rolling ball type viscometer (Figure 16). This consists of a high pressure steel chamber with a very accurately machined central barrel. The reservoir fluid is charged into this central barrel at the required pressure, and viscosity is determined by timing the passage of a steel ball through the barrel using electronic contacts. The

temperature of the viscometer is controlled by a heating jacket enabling reservoir temperature to be simulated. The roll time of the ball is proportional to the viscosity and by using pure fluids of known viscosity and density, a calibration curve may be established for the particular instrument. From this curve, the viscosity of the fluid under test is determined. The inner barrel must of course be kept scrupulously clean and to gauge at all times, after exposure to hydrocarbons.

5. Differential liberation of the gas phase from the reservoir sample

A series of simulated separator tests is made in the laboratory to establish the relationship between separator pressure and shrinkage factor, formation volume factor, liquid and gas densities and gas compressibility and solubility.

(a) Shrinkage refers to the decrease in volume of a liquid phase caused by the release of solution gas and/or by thermal contraction of the liquid (Frick, 1959). Shrinkage may be expressed as a percentage of the resulting stock tank oil (Figure 8) or as a percentage of the original volume of the liquid. It is important to remember that each reservoir oil has an 'optimum' separator pressure at a given temperature at which the shrinkage in oil volume from reservoir to stock tank conditions is minimal. If field separators can be operated at this optimum pressure, the greatest possible amount of stock tank oil will be retained from each unit volume of reservoir oil withdrawn (Kennerly, n.d.). Tank oil gravity will usually be at a maximum (i.e. most valuable) at this same separator pressure.

(b) Formation volume factor is by definition the ratio between the volume of end product (stock tank oil) and the reservoir volume of a system required to produce a unit of the end product (Frick, 1959). Formation volume factors obtained from separator tests are essential in estimating reserves. Accurate estimates are difficult to make unless reservoir oil in place can be equated to stock tank oil. The formation volume factor is therefore a means of expressing the volumetric relationship of the system.

(c) Residual oil gravity. Residual oil is a term common to PVT work to identify the liquid remaining in a cell at the completion of a differential liberation process, carried out at or near the reservoir temperature, and simulates the reservoir fluid conditions at depletion. Volume and density of these residual oils are usually reported at $60^\circ F$ and 14.7 psia.

(d) Gas solubility is defined as the number of cubic feet of gas measured at standard conditions which are in solution in one barrel of stock tank oil at reservoir temperature and pressure (Burcik, 1957). As such, it is a determination of the gas-oil ratio of a system expressed in cubic feet per barrel between the reservoir and surface.

(e) Liquid phase density is determined indirectly from the shrinkage factor (Figure 8) of the liquids in the PVT cell during a differential liberation process. After liquid density is measured at stock tank conditions, density can be calculated for each value of shrinkage at pressures between reservoir and stock tank (atmospheric pressure) at reservoir temperature. Liquid phase density values are used in reservoir engineering calculations involving material balance of fluids in a reservoir and the production therefrom, and in various recovery processes during the life of a field.

(f) Gas compressibility is determined to establish how a gas in any particular reservoir varies from the ideal gas laws, so that accurate estimates of volumes in place at reservoir conditions can be determined. Compressibility can be calculated from the analysis of a gas, but in certain cases, particularly when components such as H_2S and CO_2 are present to an extent greater than 10 percent, it is desirable to measure gas compressibility experimentally using a Burnett type apparatus shown in Figure 19.

(g) Gas gravity is the ratio of the density of a gas at atmospheric temperature and pressure to the density of air at the same temperature/pressure conditions. Gas gravity is widely used in reservoir studies to characterize natural gases, since at atmospheric pressure and temperature, the density of natural gas is proportional to its molecular weight. If the composition of a gas is known, gravities can be simply calculated with reasonable accuracy by reference to the concentration and molecular weight of each component. Gas gravity can also be determined from compressibility values or experimentally using a gas gravity (Chancel) flask.

6. Equilibrium ratios (also Equilibrium Constants) are defined as the ratio of the concentration of a component in the vapor state to its concentration in the liquid state (Frick, 1959). These values are determined by a flash liberation process in a PVT cell (Figure 14) whereby the composition of the gas and liquid in the cell are each analysed after equilibrium is reached at some pressure below saturation (bubble point) pressure, with the temperature remaining constant throughout. These values are determined for a number of pressure points between convergence pressure of the components (where the equilibrium ratio K = 1) and abandonment pressure of the reservoir. The most important use of equilibrium ratios is for the calculation of the division between vapor and liquid which occurs under equilibrium conditions at any specified temperature and pressure. The values may therefore be applied to the well stream to predict the surface recovery of liquid hydrocarbons. Also, the determination or interpretation of 'K' values defines the most efficient stage separation design on surface which will achieve maximum liquid production.

7. __Fractional analysis.__ Fractional distillation analysis of the saturated reservoir crude oil as well as analysis of the evolved gas and oil, are additional tests which are reported in PVT analysis. The analysis of the saturated reservoir crude oil gives the composition in terms of the simpler hydrocarbons present, providing information which the trained engineer can translate into expected behaviour of the producing stream. The results of low temperature fractional distillation or chromatographic analysis can also be used to calculate gas-oil ratios, stock tank oil gravities, and formation volume factors for separator pressures other than those used in the original analysis. Even bubble point pressures, liquid densities and viscosities may be calculated with reasonable accuracy from fractional analysis. Knowledge of the propane, butane, and pentane content of the reservoir oil is necessary for the design, constructions, and operation of gasoline and middle distillate plants.

Fractional distillation analysis is usually carried out in a low temperature distillation unit, whereby the increasingly heavier components are measured as they are boiled off the reservoir fluid. Component analysis of both gas and liquids from the production stream can also be determined by gas-liquid chromatography; much smaller volumes of fluid are required for accurate analysis by this method than are necessary for fractional distillation.

Gas condensate reservoirs

Until recently, crude oil reservoir systems had been studied much more extensively than gas condensate reservoirs. However, with the greater use of and requirement for natural gases and associated liquids, reservoir fluid studies of gas condensates have become increasingly important. In this country in particular, gas condensate reservoirs constitute a large portion of the hydrocarbon discoveries and an understanding of their physical and chemical characteristics is of paramount importance.

The development and operation of gas condensate reservoirs for maximum recovery requires engineering and operational methods significantly different from those of crude oil reservoirs. The most outstanding single factor about gas condensate systems is that they exist either wholly or largely in the vapor phase in the reservoir at the time of discovery. This key fact nearly always governs the development and operating program for recovery of hydrocarbons from such reservoirs. It is important for the producer to know what the phase characteristics of the reservoir fluids will be at various stages of depletion so that he can plan his separation program wisely, and minimize the loss of hydrocarbon liquids in the reservoir (retrograde condensation). Since the properties of the fluids determine the optimum engineering program, a properly engineered laboratory reservoir fluid study is imperative.

A laboratory gas condensate reservoir fluid study should include the following minimum tests:

1. Fractional distillation analysis of the field separator gas and liquid samples

2. Gas-oil ratios

3. Pressure-volume relationship of the recombined separator sample, including dew-point

4. Measurement of retrograde liquid at reservoir temperature and pressure

5. Constant volume depletion at reduced pressure including measurement of retrograde liquids and fractional distillation (or chromatographic analysis) of the gas and liquids

1. Fractional analysis

In order to determine the composition of the various phases (gas and liquid) which are being produced from a gas condensate field, it is necessary to measure the components of the stream by fractional distillation analysis. This analysis gives the production engineer information as to the type of condensation occurring at any point during production, and in turn may assist him in designing the various separation stages required from reservoir conditions to the stock tank and pipeline. Additionally, it facilitates planning of gas plant extraction equipment and maximum sale value of products under the most effective and economic production methods.

In the laboratory, fractional analysis is carried out at several stages of testing. The first stage usually involves the gas and liquid samples as received from the weel-site separator, and before recombination. Subsequently, component analyses are usually carried out on the recombined sample at various stages of pressure depletion, i.e. from reservoir to stock tank in order to determine the components of the stream at each stage.

The properties of both the liquid and gas phases which are separated from gas-condensate streams can vary considerably. One of the principal characteristics is a high methane content. Eilerts (1959) has listed the composition of gas and liquid phases of eight gas-condensate systems. The methane content of the gas phase (from field separators) varies from 83 to 92 mole percent; the hexane and 'heavies' varies from 0.4 to 0.8 mole percent. The liquid phases vary from 10 to 30 mole percent methane, and to 40 and 70 percent hexane plus. The hexane plus values are always much lower than in a crude oil system.

Hydrocarbon analysis of separator gas and liquid samples can be carried out by low temperatue fractionation (analysis) apparatus and/or gas chromatography. Gases such as hydrogen sulphide and carbon dioxide may also be determined as part of the routine gas analysis. Hydrogen sulphide in particular can be a very significant factor in the design of production facilities, because of its very corrosive nature and its effect on downstream equipment.

Gas condensate samples contain varying amounts of hexane-plus 'residues', primarily in the liquid state obtained from sampling vessels. The properties of these residues, although quite variable, can be established from:

(1)   Distillation curves of the boiling point behaviour
(2)   Component analysis
(3)   Specific gravity
(4)   Apparent or average molecular weight

Because of the increasing complexity of the fractions, component analysis beyond hexane-plus is not always carried out in PVT analysis; however, such determinations are quite helpful in predicting the overall phase, volumetric, and separation behaviour of gas condensate reservoirs.

2. Gas-oil ratios

One of the criteria for judging the nature of a hydrocarbon reservoir fluid is the gas-oil ratio of the surface separator. It is generally regarded that a gas-oil ratio less than 3000 ft^3/bl of liquid from the separator indicates a reservoir which is predominantly oil productive, the gas being evolved from the liquid. At gas-oil ratios greater than 6000 ft3/bl, the fluids are almost certainly all in the vapor phase in the reservoir, and the liquid produced is formed upon reduction in pressure and temperature during production. In the range of 3000 to 6000 ft^3/bl the state of the phase present in the reservoir cannot be predicted with any degree of certainty, except that the fluid is in the neighbourhood of its critical temperature at the reservoir temperature for that system (Eilerts, 1959).

Gas-oil ratios are usually determined at two points during laboratory PVT testing. The first stage involves the ratio of the gas and liquid samples as received from the primary separator (recombination sample). Secondly, gas-oil ratios are always measured when the recombined gas and oil samples are being subjected to production by pressure depletion from the reservoir to some abandonment pressure. The latter tests generally employ a visual high-pressure cell, somewhat similar to that used in crude oil analysis (Figure 17).

It should be pointed out that gas-oil ratios must be properly defined for satisfactory laboratory procedures, since gas-condensate systems in the field frequently undergo different types of separating procedures involving several separation stages before the final liquid phase reaches the tanks at atmospheric pressure. For purposes of studying the properties of gas-condensate fluids at reservoir conditions, it is most convenient to have a statement of gas-oil ratios and liquid output of the first stage separator through which the fluids pass. These two output streams then represent the total production of the gas-condensate fluid in the reservoir, if sampling, producing, and measuring conditions have been properly set and maintained.

3. Pressure volume relationship of the recombined sample

As already stated, laboratory PVT studies of gas-condensate systems can be carried out on recombined gas and liquid samples, generally taken at the first-stage separator at the well site. When component analysis is to be carried out by low temperature distillation, recombined samples are favoured because they supply the necessary large volumes required for that type of test. However, with the advent of gas-liquid chromatography and its application to component analysis of the liquid fractions, a much smaller volume is required, and bottom hole samples of gas-condensate reservoirs can be satisfactorily utilized.

Some operators, however, still prefer to use recombined samples because bottomhole samplers always run the risk of picking up excess fluids clinging to the production tubing during the trip to and from bottom.

If recombined samples are to be used, it is necessary that accurate measurements of hydrocarbon gas and liquid production rates are obtained during well conditioning and sampling, since subsequent laboratory tests will be based on these ratios. If (produced) gas-condensate ratios established from field measurements are in error by as little as 5 percent, the dew (condensation) point from the laboratory tests may be in error by as much as 100 psi (Frick, 1959).

The pressure-volume relationship of a recombined sample is obtained in a windowed cell (Figure 17). This cell is generally of 400 to 500 ml. capacity and is capable of withstanding (about) 10 000 psi maximum pressure. The recombined or bottomhole sample is charged to the cell in the correct gas/liquid proportions; the pressure is increased in steps to some value above the dew point, using a mercury pump for this purpose.

During the test, the cell is kept at a prescribed reservoir temperature. While the pressure is being raised under constant temperature conditions, the operator views through the cell windows, the relative volume of the fluid level at each pressure step as well as the dew or condensation point (the point at which the system changes to a complete single-phase vapor state). The pressure is then held at reservoir pressure and the amount of 4. retrograde liquid which may be present in the cell is noted. Windowed cells are so constructed that an operator can measure liquid volumes in the cell as small as 0.05 ml.

A series of isothermal pressure-volume determinations provides the basic information from which a phase diagram (Figure 18) can be plotted. This is to aid in visualizing conditions in the reservoir and the processes that occur when fluid is removed from the reservoir to the surface. More extensive tests can be made for systems of modified composition, such as gradations from dry injection gas through intermediate compositions (mixtures of dry and reservoir gas) to original reservoir composition. They help to determine whether the system might be near its critical region and also show the relationship of the dew point pressure to composition at reservoir temperature.

Referring to the phase diagram in Figure 18, with the reservoir temperature indicated, the maximum retrograde condensation resulting from a flash equilibrium process approaches 13 percent. The original reservoir fluid may exist as a single phase fluid such as at A; as a dew-point gas phase such as at B; or it may exist at a pressure less than B in the two-phase region, for example, at D. Since the condensation required to produce liquid flow in the reservoir is not exceeded, a single-phase fluid enters the well-bore. The liquid phase produced at E results from the retrograde condensation and, to some extent, the reduction in temperature of this single-phase fluid (Kobayashi, 1958).

5. Constant volume depletion at reduced pressure

Pressure depletion tests can be made on a gas-condensate reservoir fluid in the laboratory in such a manner as to simulate pressure depletion of the reservoir, on the assumption that condensing retrograde liquid appearing during pressure reduction will remain immobile in the reservoir. This assumption is valid in those cases for which the volume of condensation is too low to provide significant relative permeability to the retrograde fluid. However, in some other cases, reduction of pressure isothermally will condense relatively large volumes of liquid in the pores of the reservoir raising the liquid saturation to the point where some liquid will migrate to producing wells. In this case, the application of relative permeability curves to the particular rock-liquid system may be required to comprehend the particular behaviour of the reservoir under a planned producing condition.

The actual test procedure for simulating pressure depletion (with immobile reservoir liquid) in a laboratory visual cell (Figure 17) is to place the properly recombined reservoir fluid of known total composition in the cell at original reservoir pressure and temperature. Maintaining the cell volume and temperature constant (to simulate a constant volume reservoir), pressure is reduced in 500 psi increments by removing gas from the system. The resultant volume of gas and liquid (below the dew point) remaining in the cell is then measured, as well as the volume and composition of the produced fluid. The analysis of the produced fluid yields composition information for calculating the condensible liquid content of the gases produced at all stages of pressure depletion.

The stepwise pressure depletion tests are usually carried to some level representing the abandonment pressure of the reservoir, after which the quantity and composition of the fluids remaining in the cell are determined. This provides a means of checking the quantity of each component produced in the gas during pressure depletion, since original composition is known.

It should be noted that in the case of samples, the composition of which is to be determined by low temperature distillation, it is necessary to use a larger volume than that provided by the visual cell already described. In this situation, a 'blind' cell of approximately 2000 ml. capacity is substituted for a repeat run after visually determining the critical properties of the sample in the visual cell.

The **compressibility** or **gas deviation** factor can be calculated for a produced gas of varying composition from the data obtained during the pressure depletion tests described previously. However, where accurate metering and pressure drop calculations are required, the calculated method is usually not of sufficient accuracy, and the deviation must be measured experimentally using a compressibility apparatus as in Figure 19. This enables the actual volume/pressure relationship of a sample to be determined isothermally. This measurement may be of particular significance where gases such as CO_2 and H_2S are present in the system, as these components can have a marked effect on the deviation of natural gas systems, causing considerable errors in calculated gas recoveries unless the gas deviation factor is determined experimentally.

III. CONCLUSIONS

The foregoing discussion has presented the main experimental procedures used in a PVT laboratory for the study of the physical and other compositional properties of petroleum reservoir fluids. These techniques require high standards of accuracy and expertise by the operating personnel; sampling of the reservoir fluids in particular must be carried out with care and foresight, for on this, the accuracy of the resultant analysis depends.

The data obtained from the analysis enable the reservoir engineer to predict the present and future reservoir fluid phase behaviour of a hydrocarbon deposit. This includes such aspects as changes in fluid phase composition, density, and viscosity attendant to field pressure reduction resulting from natural depletion and/or pressure maintenance by fluid injection, gas cycling etc.

In a world increasingly short of energy, reservoir fluid analysis should be a mandatory part of engineering studies preluding any hydrocarbon production, to ensure the maximum efficient recovery of all petroleum reserves.

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NOTE: All diagrams courtesy of Ruska Instrument Corporation
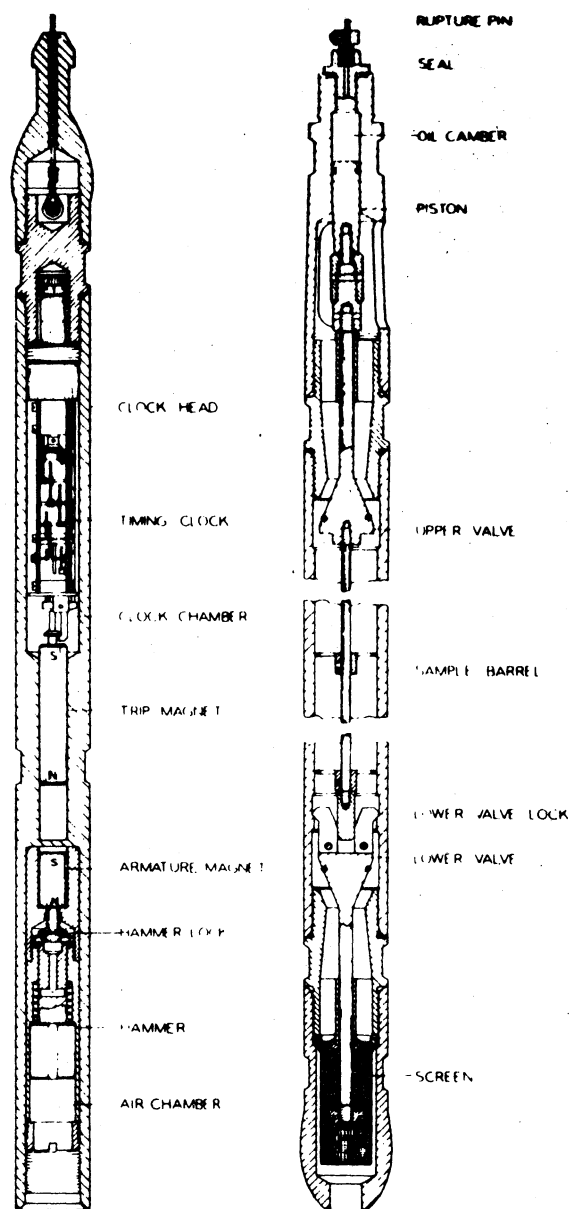
Figure 1 **CROSS SECTION, SUBSURFACE SAMPLER**

Labels (left assembly, top to bottom):
CLOCK HEAD
TIMING CLOCK
CLOCK CHAMBER
TRIP MAGNET
ARMATURE MAGNET
HAMMER LOCK
HAMMER
AIR CHAMBER

Labels (right assembly, top to bottom):
RUPTURE PIN
SEAL
OIL CHAMBER
PISTON
UPPER VALVE
SAMPLE BARREL
LOWER VALVE LOCK
LOWER VALVE
SCREEN

BUBBLE POINT PRESSURES— PVT SAMPLE

FIGURE 2

PRESSURE IN SAMPLER (PSIG)

MERCURY FUNNEL

SHIPPING BOTTLE

SAMPLE

TRANSFER PUMP

BLEED VALVE

UPPER TRANSFER HEAD

MERCURY

SAMPLE CHAMBER

LOWER TRANSFER HEAD

BLEED VALVE

SCHEMATIC DIAGRAM, TRANSFER MECHANISM

Figure 3
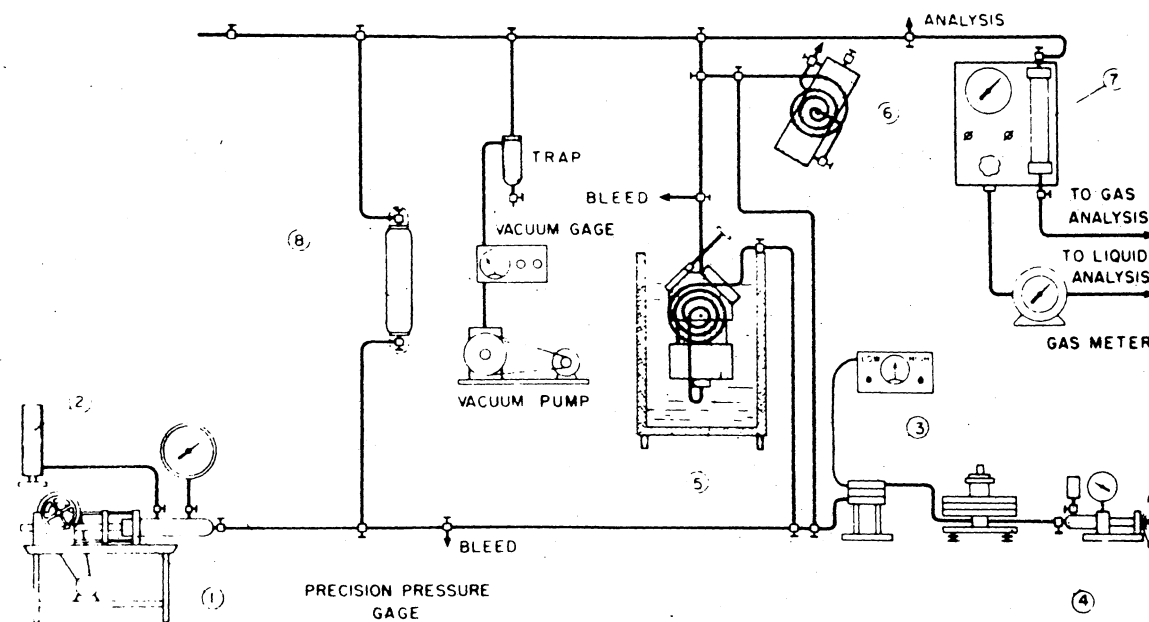
FIGURE 4 EQUIPMENT FOR THE STUDY OF SUBSURFACE SAMPLES

1. Volumetric Pump,   2. Mercury Tank,   3. Differential Pressure Indicator,   4. Dead Weight Gage with Hand Pump, 5. Windowed Liquid Phase Cell in Thermostatically-Controlled Oil Bath, 6. Viscosimeter, 7. Equilibrium Flash Separator, 8. Subsurface Sampler, or Sample Shipping Bottle.

Figure 5
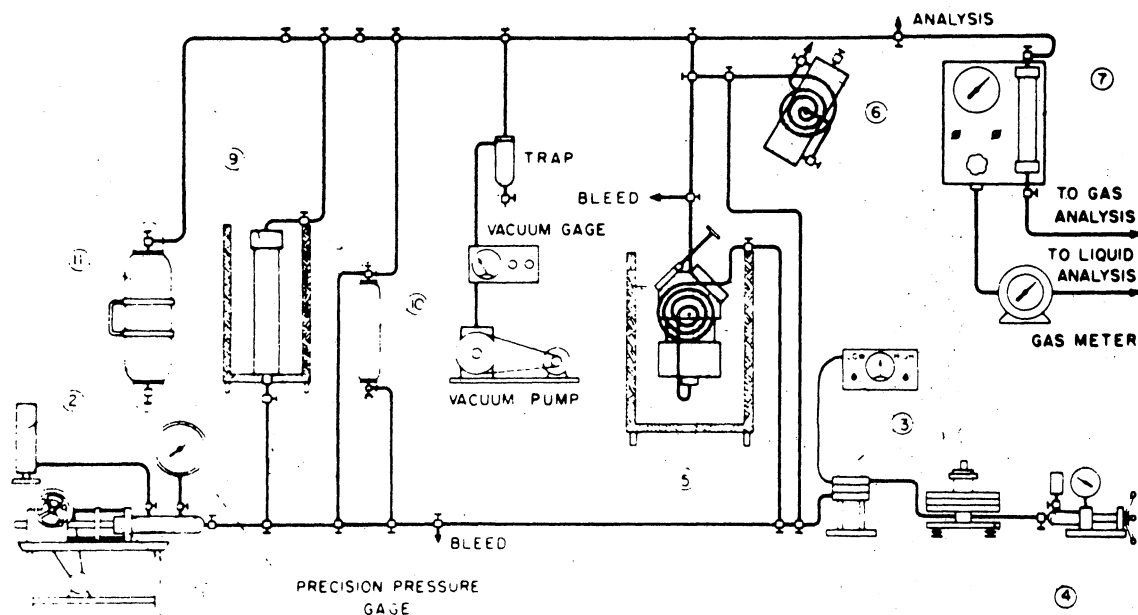
EQUIPMENT FOR THE STUDY OF RECOMBINED SAMPLES

1 Volumetric Pump, 2 Mercury Tank, 3 Differential Pressure Indicator, 4. Dead Weight Gage with Hand Pump, 5. Windowed Liquid Phase Cell in Thermostatically-Controlled Oil Bath, 6. Viscosimeter, 7 Equilibrium Flash Separator, 9. Recombination or Storage Cell in Thermostatically-Controlled Oil Bath, 10 Separator Oil Sample Bottle, 11 Separator Gas Sample Bottle
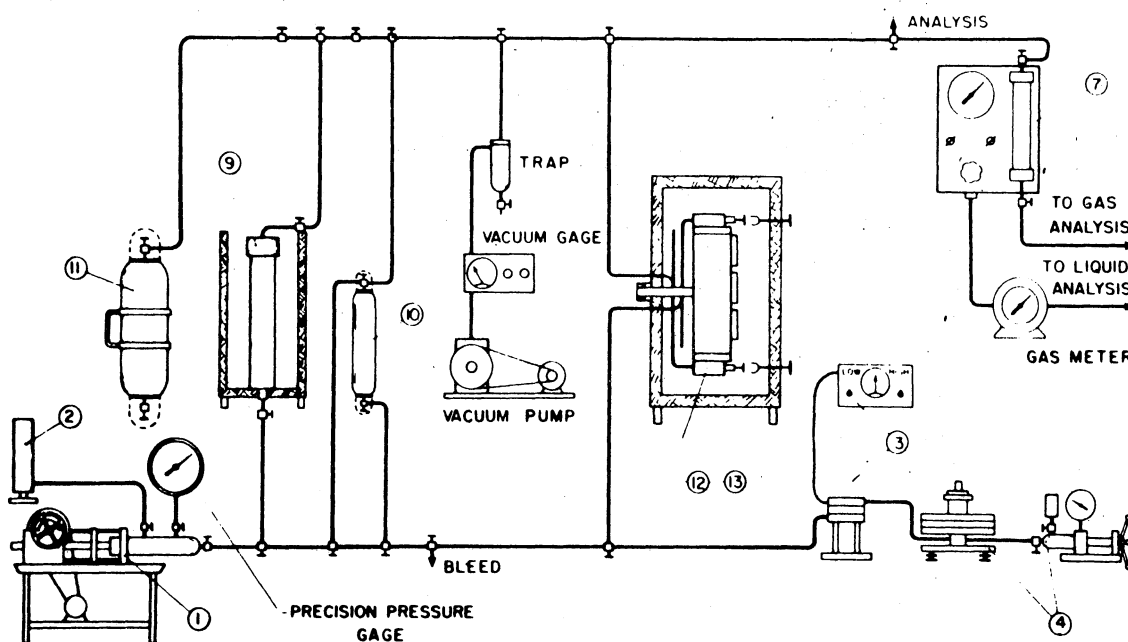
EQUIPMENT FOR THE STUDY OF CONDENSATE SAMPLES

1. Volumetric Pump, 2. Mercury Tank, 3. Differential Pressure Indicator, 4. Dead Weight Gage with Hand Pump, 7. Equilibrium Flash Separator, 9. Recombination or Storage Cell in Thermostatically-Controlled Oil Bath, 10. Separator Oil Sample Bottle, 11. Separator Gas Sample Bottle, 12. Windowed Condensate Cell, or 13. Blind Expansion Cell in Thermostatically-Controlled Air Bath.
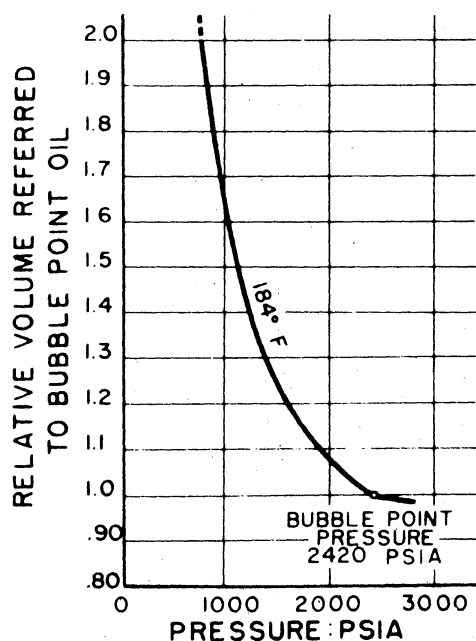
FIG. 6. COMPRESSIBILITY OF
CONSTANT WEIGHT OF CRUDE OIL -
NATURAL GAS MIXTURE
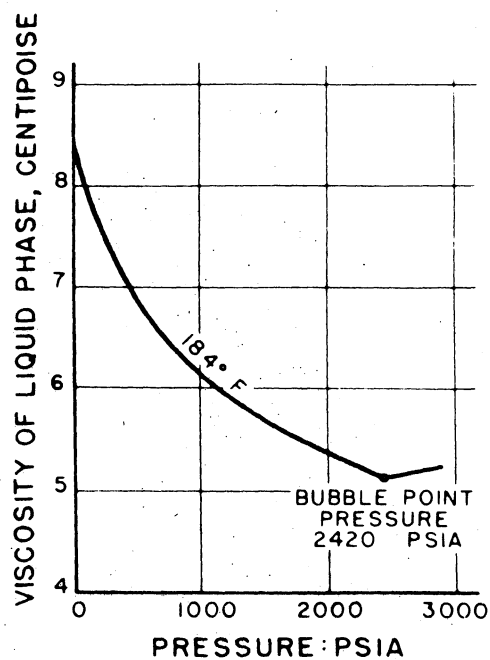
FIG. 7. VISCOSITY OF LIQUID
PHASE AS A FUNCTION OF PRES-
SURE
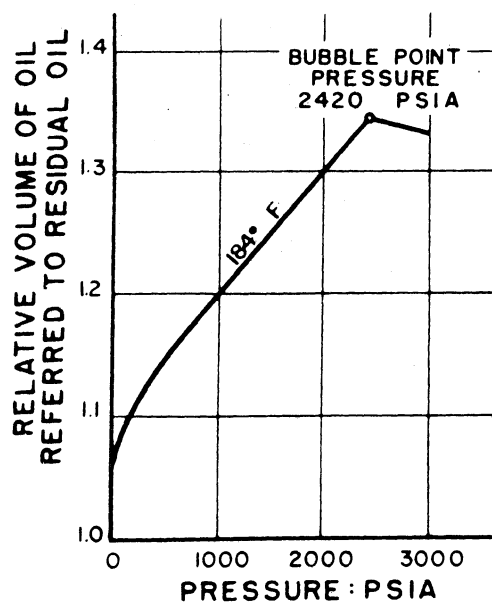
FIG. 8. SHRINKAGE OF LIQUID
PHASE
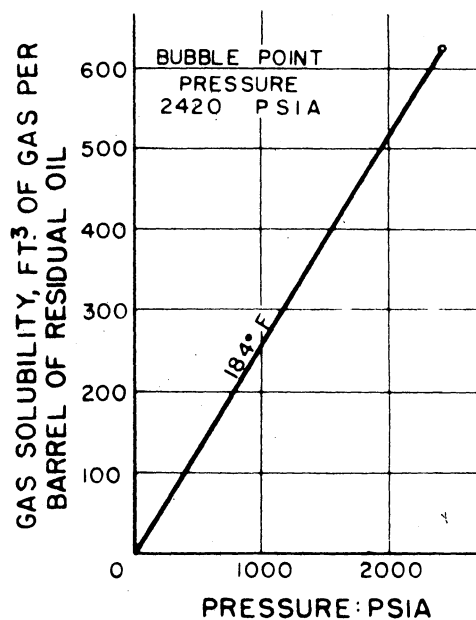
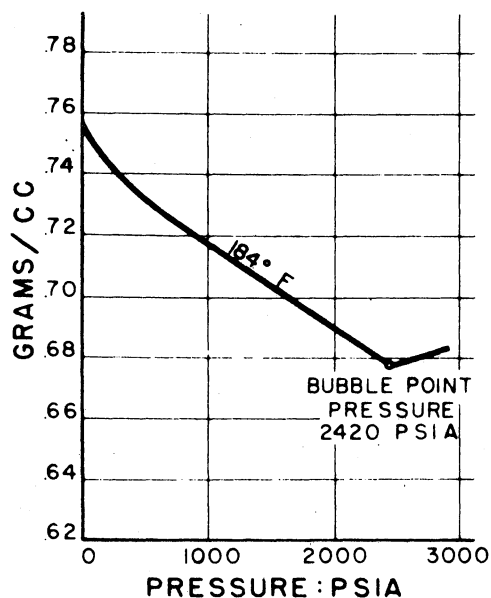

FIG. 9. GAS SOLUBILITY IN
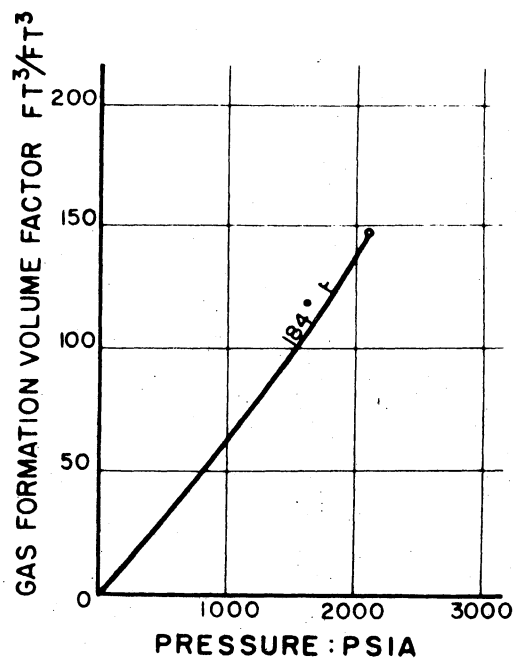LIQUID PHASE

FIG. 10. DENSITY OF LIQUID
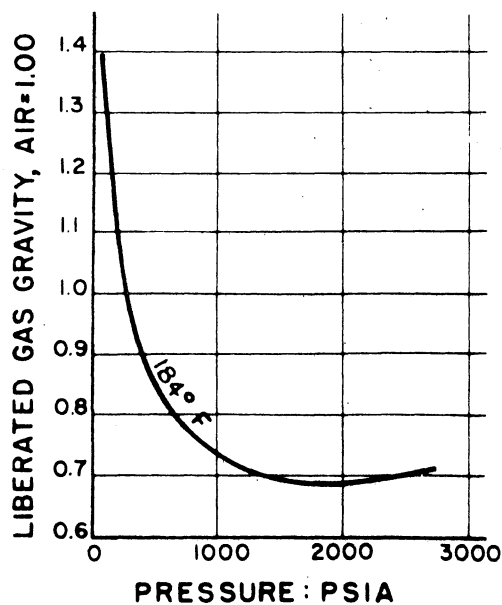PHASE

FIG. 11. COMPRESSIBILITY OF
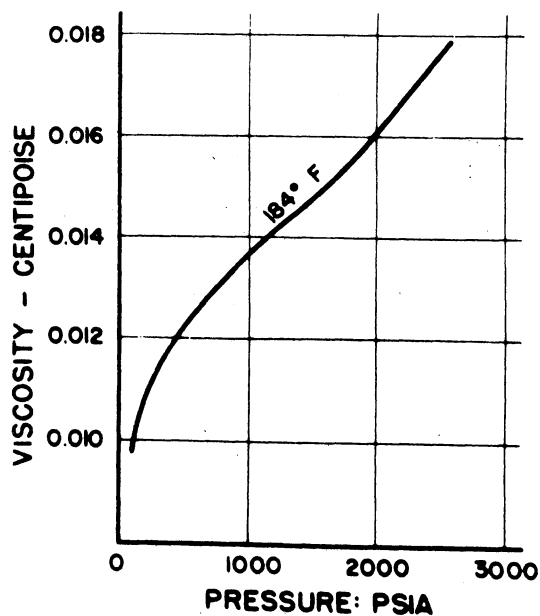LIBERATED GAS PHASE

FIG. 12. GAS GRAVITY OF LIBER-
ATED GAS PHASE

FIG. 13. CALCULATED VISCOSITY OF
LIBERATED GAS

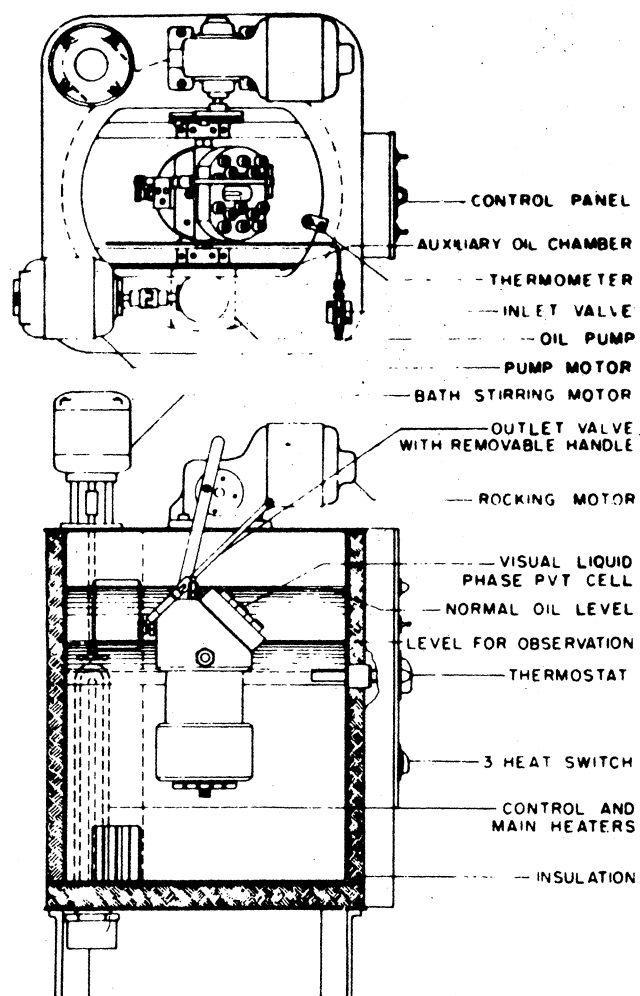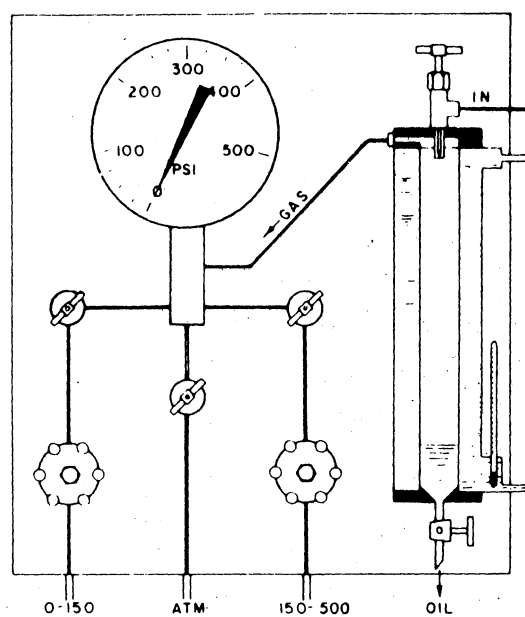CONTROL PANEL

AUXILIARY OIL CHAMBER

THERMOMETER

INLET VALVE

OIL PUMP

PUMP MOTOR

BATH STIRRING MOTOR

OUTLET VALVE
WITH REMOVABLE HANDLE

ROCKING MOTOR

VISUAL LIQUID
PHASE PVT CELL

NORMAL OIL LEVEL

LEVEL FOR OBSERVATION

THERMOSTAT

3 HEAT SWITCH

CONTROL AND
MAIN HEATERS

INSULATION

Figure 14   VISUAL LIQUID PHASE PVT CELL IN
CONSTANT TEMPERATURE OIL BATH

Flow Diagram, Flash Equilibrium Separator

Figure 15

SOLENOID

BARREL SEAL

GAS CHAMBER

PIVOT

POSITIONING STOPS

LATCH

INLET

OUTLET

STAINLESS STEEL MEASURING BARREL

INSULATING JACKET

HEATING ELEMENT

THERMOCOUPLE

STEEL BALL

PRESSURE HOUSING
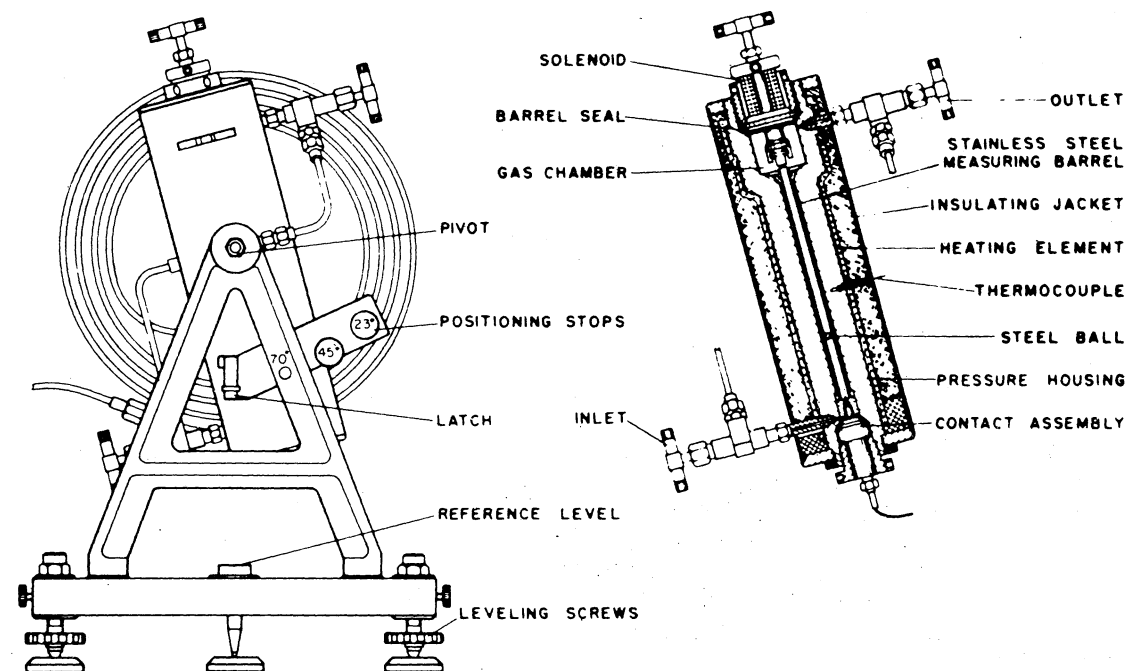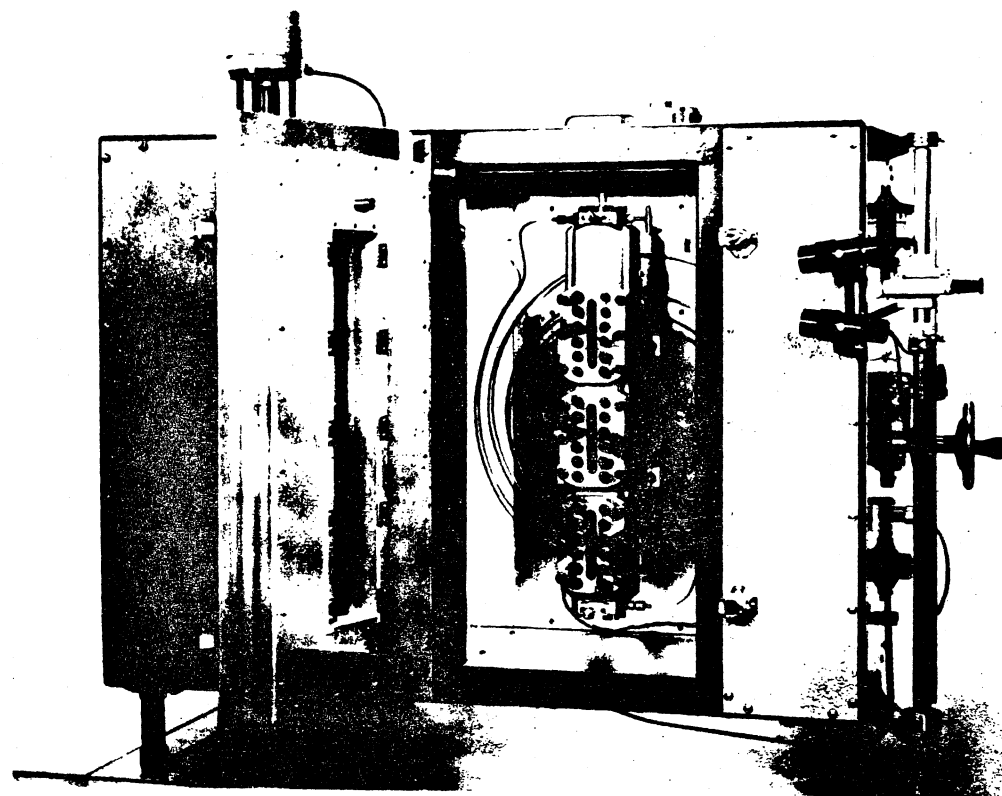
CONTACT ASSEMBLY

REFERENCE LEVEL

LEVELING SCREWS

FIGURE 16 HIGH PRESSURE ROLLING BALL VISCOSIMETER

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M(G)359

THREE WINDOWED CONDENSATE CELL AND BATH
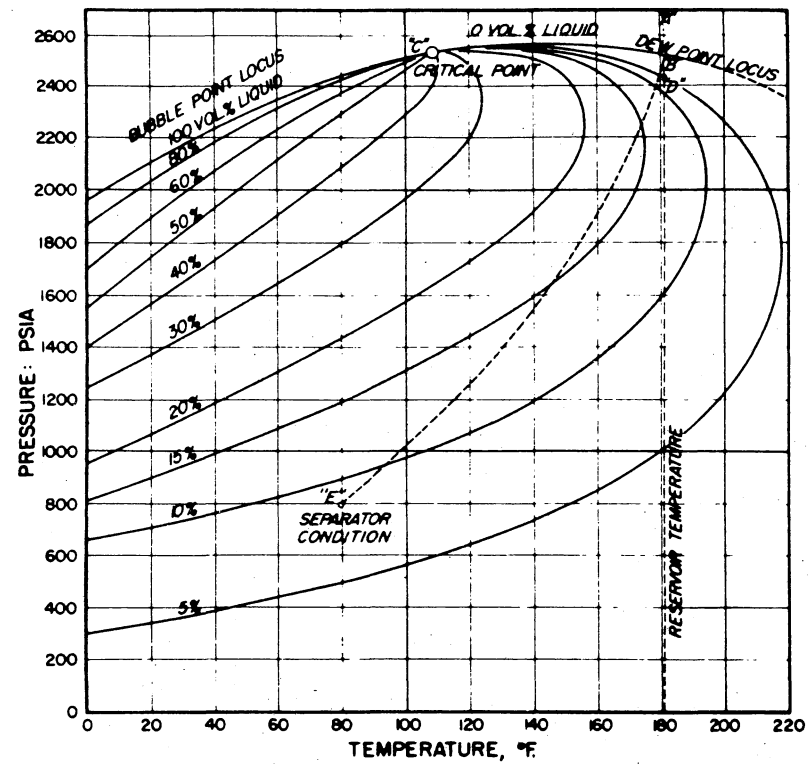Figure 17

FIG. 18. PHASE DIAGRAM FOR A NATURAL GAS — NATURAL
GASOLINE MIXTURE

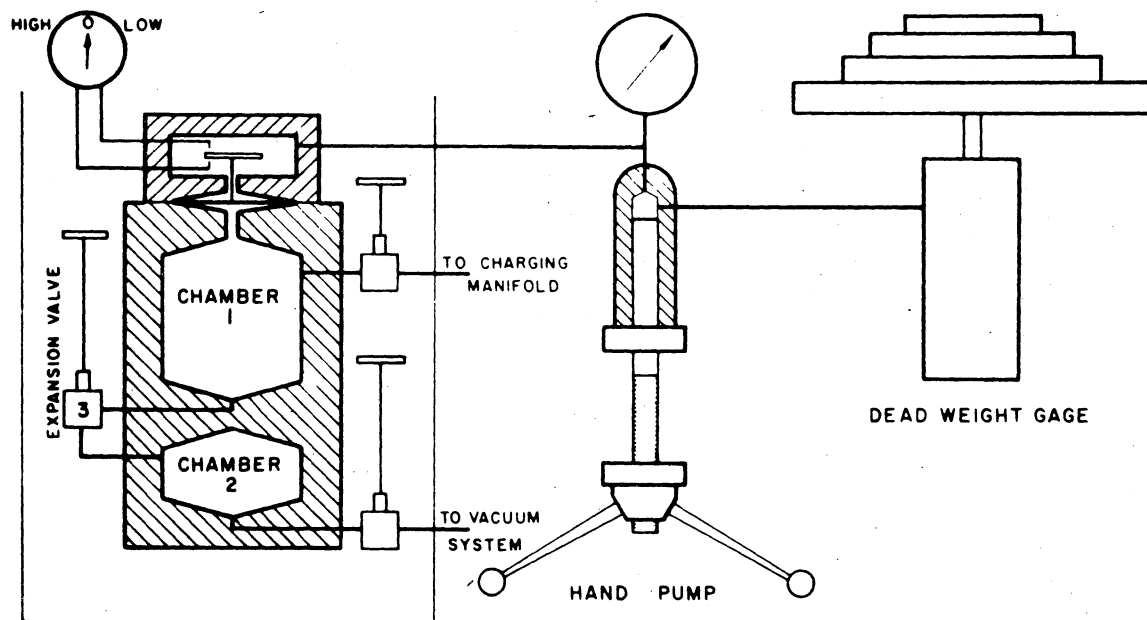To accompany Record 1973/169   M(G)362

FIGURE 19 **COMPRESSIBILITY APPARATUS FOR GAS LAW DEVIATION**

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M(G)361