STUDIES OF THERMAL AND PHYSICAL PROPERTIES OF HYDROCARBONS

Thesis by
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In Partial Fulfillment
of the
Requirements for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1934

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General Introduction

The work reported in this thesis was carried out during the last three years at the California Institute of Technology as part of Research Project 37 of the American Petroleum Institute. The general purpose of the investigation is the study of the fundamental properties of hydrocarbon mixtures which control their retention in underground formations.

The work of earlier investigators had indicated that rather large changes in the physical properties from those observed at atmospheric pressure took place when natural hydrocarbon mixtures were at equilibrium under the pressures and temperatures found in many natural reservoirs. As the physical properties such as viscosity, density, etc. have a large effect on the retention of the oil in a natural reservoir, a study of the more important of them was undertaken by the American Petroleum Institute. The work of Project 37 has been restricted to measurements of the composition, rate of solution, density, change in volume, specific heat, viscosity of hydrocarbon mixtures as a function of pressure and temperature. The derived thermal properties are of interest in the determination of the available energy of a natural reservoir.

The work reported in this thesis consists of a description of the apparatus used in the general study of the physical properties of hydrocarbon mixtures under equilibrium conditions, and of complete equilibrium data on the system composed of methane and propane, and of complete pressure-volume-temperature and thermal data on pure propane. Both studies covered most of the pressure and temperature ranges encountered in underground formations.

Reprinted from
INDUSTRIAL AND ENGINEERING CHEMISTRY
Vol. 26, Page 103, January, 1934

Phase Equilibria in Hydrocarbon Systems

I. Methods and Apparatus

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Apparatus and methods for studies of phase equilibria in hydrocarbon mixtures at pressures up to 200 atmospheres in the temperature range from 20° to 100° C. are described. The data obtained permit the prediction of the density, composition, and relative mass of each phase present when a mixture of any total composition is brought to equilibrium at any set of temperature and pressure conditions within the range studied. Subsequent articles of this series will present data for both simple and complex mixtures.

A KNOWLEDGE of the behavior of complex hydrocarbon systems under equilibrium conditions corresponding to those found in underground petroleum reservoirs is of primary importance to the petroleum production technologist. The simpler examples of such systems are also of interest from the purely scientific point of view.

The aim of this work was to follow the behavior of gaseous and liquid phases present in equilibrium at temperatures ranging from 20° to 100° C. (68° F. to 212° F.) and at pressures from 1 to 200 atmospheres (approximately 15 to 3000 pounds per square inch absolute). In order to ascertain completely the state of the system, measurements of the density, volume, and composition of each of the phases present were required. These measurements were made over a series of temperatures, pressures, and total compositions in order that the effect of these variables might be determined.

The equilibrium method used in this work resolved itself into the following steps: the measurement of the amount of an original liquid phase placed in an equilibrium vessel, the measurement of a series of quantities of gaseous material and their quantitative compression into the equilibrium vessel, the attainment of equilibrium, and the determination of the state of the system after each addition of material.

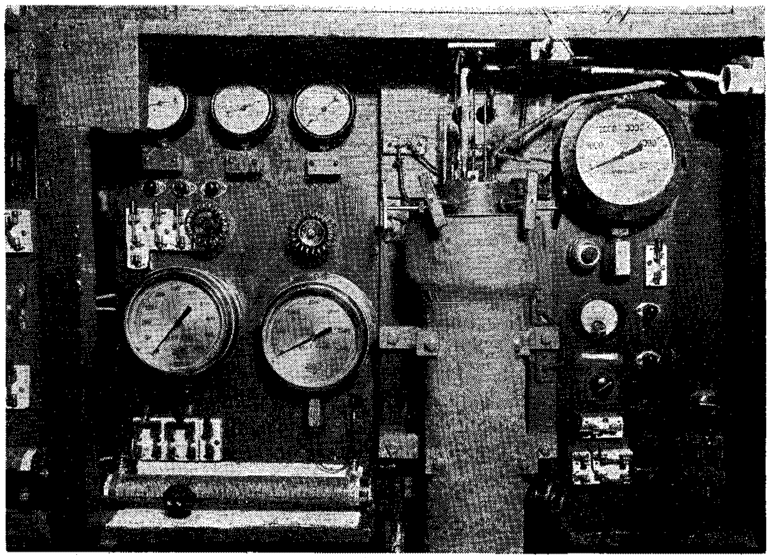

FIGURE 1. COMPRESSOR AND CONTROL PANEL

MEASUREMENT OF ENTERING MATERIALS

Relatively nonvolatile liquids were measured by weighing a suitable container before and after pouring the sample into the equilibrium vessel. The latter was then closed and connected for use. If the liquid was a pure substance of volatile character, a portion of it was distilled into the equilibrium vessel from a weighed container. Volatile complex liquids were cooled to a sufficiently low temperature to be handled by the method used for nonvolatile liquids.

Gases entering the system were measured by withdrawing from a calibrated reservoir of constant volume and noting the resulting drop in pressure. The sample bomb containing the gas supply was heated in a diethylene glycol bath to a sufficiently high temperature to insure complete vaporization. That the temperature used was high enough could be verified by determination of the dew point of the gas at the pressure existing in the sample bomb, as described below. The gas was then admitted, through heated tubing lines, to the reservoir bomb in a diethylene glycol bath carefully thermostated at 100.0° C. The reservoir was so calibrated that the quantity of gas in it was known for any given pressure up to a maximum of about 20 atmospheres. The calibration was made for each gas

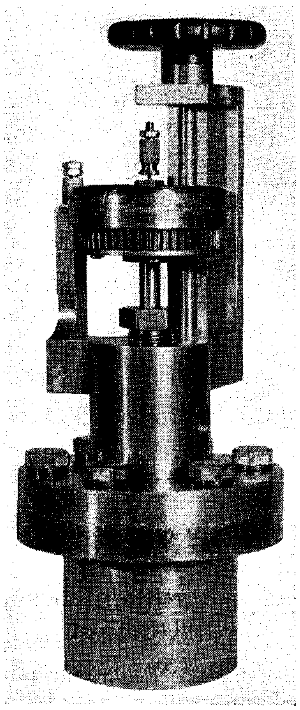

Figure 2. Equilibrium Cell

by filling to nearly maximum pressure, drawing off successive portions of gas into a mercury buret for measuring the volume at atmospheric pressures, and noting after each withdrawal the pressure in the reservoir. The buret was located in an air bath maintained at 40.0° C. (104.0° F.) by a thermostat control. The density of the gas was measured by means of an Edwards gas density balance placed in the same air bath. Having obtained this calibration, the mass of gas withdrawn from the reservoir for use in the equilibrium system could be determined from the reservoir pressure reading before and after withdrawal.

The gas pressure in the reservoir was measured by a fluid pressure scale connected to the reservoir by an oil-filled tube. The gas was kept from contact with this oil by interposing a mercury U-tube. The volume of the reservoir was kept constant within 0.005 ml. (in a total volume of 175 ml.) by forcing in or withdrawing oil from the connecting tube with a screw plunger, the correct volume being indicated by the flash of a signal lamp operated through a pointed contact just above the mercury surface on the oil side of the U-tube. A shut-off valve was installed in the bottom of the U in order that the reservoir might be evacuated without disturbing the pressure-measuring system. The fluid pressure scale used was a modified Crosby instrument having a range from atmospheric pressure to 300 pounds per square inch (20 atmospheres), readings being reproducible to 0.1 pound per square inch.

This method of gas measurement was successfully used for gases ranging in composition from methane to untreated natural gas from the well. The variation of different calibrations for the same gas was less than 0.2 per cent. The reservoir was also useful for determination of compressibility factors of gases at pressures up to 200 atmospheres, by the method developed at the U. S. Bureau of Standards.[1]

Compression of Gases

The gases used were measured at relatively low pressures (below 20 atmospheres) to avoid partial condensation. After measurement it was necessary to compress the measured samples quantitatively into the equilibrium vessel without contamination or absorption by such materials as lubricants. The equipment used was a compressor in the form of a steel buret provided with gas inlet and outlet valves at the bottom. The measured quantity of gas was drawn in from the reservoir. Mercury was then forced into the compressor by a steam-driven plunger pump. When the gas in the top of the compressor was compressed to a pressure exceeding that in the equilibrium cells, the gas outlet valve was opened and the gas forced into the cell. The level of the mercury was followed in the lower part of the buret by signal lights connected to insulated contacts in the wall of the compressor. To secure a minimum clearance volume (1.5 ml. in a total volume of 1500 ml.), the upper part of the compressor was constricted to about 4.8 mm. in diameter. In this tube was suspended a small carbon rod. As the mercury rose in the tube, the resistance between the upper end of the carbon rod and the mercury was reduced. A bridge circuit, one arm of which was the carbon rod, enabled one to follow the level of the mercury in the tube. This made it possible for the operator to make the stroke of the pump accurately reproducible. The gas inlet and outlet valves were integral with the upper end of the tube.

As there was possibility of partial liquefaction of the gases if the compression were done at room temperature, the entire compressor was electrically thermostated at 100° C. A photograph of the compressor and the accompanying control panel is shown in Figure 1. The apparatus was always so operated that the pressures were kept well below the dew point of the gas in the pump at the time. By care in this regard the possibility of condensation in the compressor was avoided. For the same reason the lines connecting the compressor with the reservoir and with the equilibrium cell were electrically heated to 100° C. Their temperature was measured by small thermocouples soldered to the lines.

Equilibrium Cell

Equilibrium was attained in a steel bomb (Figure 2) whose inside diameter was 2 inches (5.08 cm.), with an inside depth of 2.5 inches (6.35 cm.). The top was bolted to the body of the cell, a soft metal gasket being used to make a tight joint. Relatively nonvolatile liquids were placed in the bomb before closing, while gases were admitted through a connection in the top. At the end of a run the material in the system was removed by loosening a specially designed blow-off plug in the bottom of the bomb. When tight, this plug was just flush with the inside bottom surface of the bomb and so prevented any hydrocarbon material from being trapped or segregated. This bottom blow-off was found very useful, since relief of pressure through the top carried particles of liquid phase mechanically into the connecting lines, owing to frothing upon release of dissolved gas.

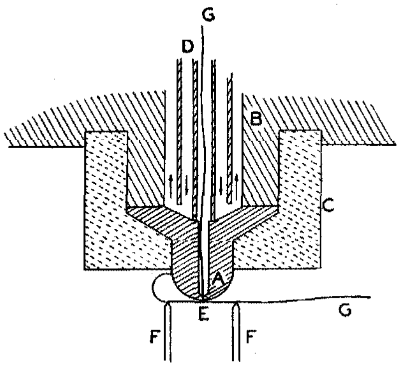

Figure 3. Dew Point Apparatus

In order to bring the contents of the bomb to equilibrium rapidly, it was mounted on a bell crank which was oscillated through an angle of about 60° by an electric motor drive. This mounting kept the body of the bomb submerged in an oil bath which was automatically controlled to the temperature at which measurements were being made.

Since the inside of the bomb was made accurately cylindrical, a measurement of the height of liquid at any time when the bomb was in a vertical position gave a measure of the volume of the liquid phase. To measure the position of the liquid surface, a short piece of 1.5-mil platinum-iridium wire was mounted at right angles to the axis of the cylindrical bomb on two needle points on the end of a micrometer screw. An electrical connection from one end of the wire was brought out of the bomb through an insulating sleeve in the micrometer screw. The other end of the small wire was grounded to the bomb. During operation a small current (200 milliamperes) was passed through this wire, raising its temperature slightly above that of its surroundings. If the micrometer was gradually screwed down until the wire touched the liquid surface, its temperature, and hence its electrical resist-

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[1] Bean, H. S., *Bur. Standards J. Research*, 4, 645-61 (1930).

ance, was suddenly changed. The resistance of the small wire, as indirectly measured by a simple potentiometer circuit, gave a suitable indication of this change, and thus the position of the liquid surface could be accurately located and a reading of the micrometer made. Readings of the position of the liquid surface were easily reproducible to 0.001 inch (0.0254 mm.) by this method.

Pressures within the equilibrium cell were measured by means of another fluid pressure scale whose range was from atmospheric pressure to 3000 pounds per square inch (approximately 200 atmospheres), readings being reproducible to one pound per square inch. This scale was connected to the equilibrium system by an oil-filled line and mercury U-tube similar to that of the reservoir system described. The calibration of the fluid pressure scale was checked by comparison with the vapor pressures of pure carbon dioxide and pure propane at known temperatures.

Since some of the gas measured and compressed into the equilibrium system did not pass into the equilibrium cell, it was necessary to know the amount of gas required to fill the connecting lines and the gas side of the mercury U-tube to any pressure within the working range. This portion of the system was always maintained at 100.0° C. to avoid condensation therein. The determination of this correction, to be deducted from the amount of gas in the system, was made directly by compressing known amounts of the gas in question into the lines, with the valve at the entrance to the equilibrium bomb closed, and measuring the pressures. This correction amounted to about 10 per cent of the total quantity of gas measured but could be determined with good accuracy.

Dew Point Apparatus

Dew point determinations furnish information which is useful in locating boundary conditions between the one- and two-phase portions of these equilibrium diagrams. The apparatus used for such determinations consisted of a pressure cell built into a steel block whose temperature was thermostatically controlled. The essential features of this apparatus are shown in Figure 3. A hemispherical copper tip, *A*, 3 mm. in radius, was supported from the steel cell top, *B*, and the supporting parts were covered by the heat-insulating shell, *C*. This tip was kept at constant temperature by circulating thermostated oil in contact with its upper surface through the concentric tubing lines, *D*. The walls of the cell were held at a somewhat higher temperature (3° to 4° C. higher) in order to prevent condensation on them. Approximately 0.1 mm. below the copper tip was supported upon the electrically insulated points, *F*, a copper-constantan thermocouple, *E*, of No. 40 B & S gage wire. This junction was prepared by carefully silver-soldering the wires exactly end-to-end in a hydrogen atmosphere. Another couple was located just inside the surface of the tip. Since the suspended junction was at a slightly higher temperature than the cooled tip, the difference in temperature could be indicated by including both couples through the leads, *G*, in a closed circuit with a sensitive galvanometer. The actual temperature of the copper tip was measured by the internal couple and a potentiometer.

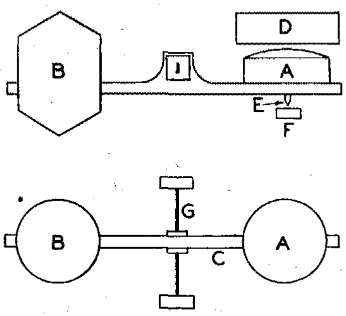

Figure 4. Elevation and Plan of Gas Density Balance

A. Copper plummet containing movable solenoid
B. Aluminum plummet
C. Aluminum beam
D. Stationary solenoid
E. Contact point
F. Mercury cup
G. Torsion suspension

The dew point determination was made by slowly compressing the gas sample into the cell until a small amount of liquid formed on the copper tip thus bridging between the tip and the suspended couple and decreasing the temperature difference between them. This caused a sudden deflection of the galvanometer mirror which was easily noticeable. A pressure reading having been taken, the pressure in the cell was then slowly decreased until the liquid just disappeared from the tip, and the pressure was again read. The final pressure was taken as the mean of several readings at disappearance of liquid, which differed ordinarily by only about 1 pound per square inch or about 0.1 atmosphere from the pressure at which liquid formed.

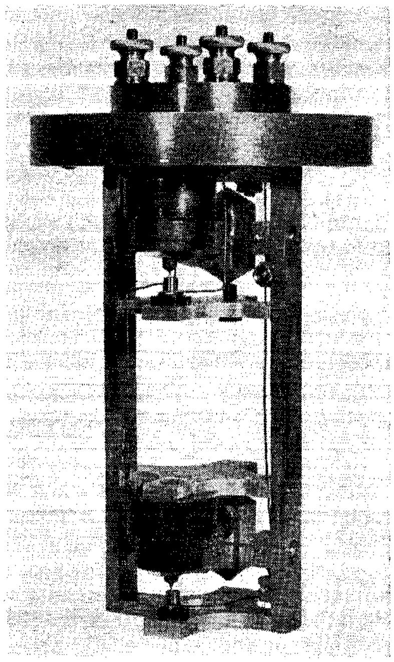

Figure 5. Density Balance Assembly

Density Apparatus

In the study of complex mixtures, such as those found in petroleum pools, two phases are almost always present, and measurements with the equilibrium cell and dew point apparatus are not sufficient to determine fully the state of the system. This necessitates direct measurement of the density of each of the phases.

A type of density balance was developed for the measurement of both gas and liquid densities at equilibrium pressures up to 200 atmospheres. Two schematic views are shown in Figure 4. The aluminum beam (8 cm. in length) carries on one end an aluminum plummet and on the other a copper plummet. As the volumes of the plummets are unequal, the masses being approximately equal, the force required to keep the beam in balance is a function of the density of the fluid in which the balance is immersed. This restoring force was supplied by two repelling solenoids, one of which was placed within the copper plummet and the other mounted directly above it in a stationary copper housing. A measurement of the current flowing through the two coils in series when they held the beam in balance gave an indication of the density of the fluids. The beam was supported by a light steel torsion mounting, the two members of which also served as electrical leads to the movable solenoid. The position of balance was indicated by the flash of a signal lamp connected in series with the platinum contact point and the mercury surface in the cup. The current (100 to 300 milliamperes) flowing through the coils was determined by means of a potentiometer which measured the voltage drop across a standard resistance placed in the circuit.

Two such balances, one for the gas phase and one for the liquid phase, were mounted, one above the other, in a frame suspended from the removable top of a pressure cell. A photograph of this assembly is shown in Figure 5. A centrifugal agitator was provided in the bottom of the pressure cell to secure equilibrium between the two phases. The entire cell was immersed in an oil bath whose temperature was carefully regulated. The equilibrium pressure was measured by a fluid pressure scale connected to the inlet line by a mercury U-tube trap similar to those previously described.

Since the relation between the flow of current through the coils and the density of the fluid was somewhat complicated, the balances were directly calibrated by immersing them in liquids and gases of known densities and measuring the current required to bring the beams into balance. A sample calibration curve of the gas density balance is shown in Figure 6. For this calibration carbon dioxide under varying pressures was used, the density of carbon dioxide being determined by measuring its compressibility under the same conditions of temperature and pressure as those at which the balance was calibrated.

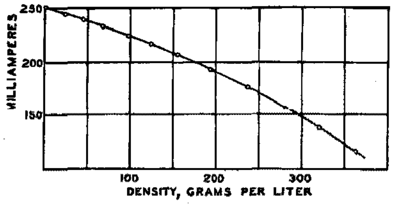

FIGURE 6. DENSITY BALANCE CALIBRATION CURVE

APPLICATION TO COMPLEX MIXTURES

When studying a complex mixture of crude oil and natural gas, the oil was weighed into the equilibrium cell and its volume and vapor pressure were measured at the desired temperature. A measured quantity of natural gas was then admitted from the reservoir through the compressor. The equilibrium cell was agitated until the pressure remained constant. After each addition of gas the equilibrium pressure and the volume of the liquid phase were measured. The additions of gas were continued until the maximum desired saturation pressure had been reached. From these data were obtained the total mass of material and the volume of each phase, but the densities and the compositions were still undetermined. The densities of the two phases were determined by carrying out measurements under identical conditions of temperature and initial concentration of oil in the density balance apparatus. The mass present in each phase could then be calculated from its volume and density.

Since the exact compositions of the crude oils themselves would be very difficult to determine, no attempt was made to ascertain the composition of the liquid phase. The composition of the natural gas used was determined by low-temperature fractionation analysis. By careful manipulation to take advantage of the strong tendency for these hydrocarbon solutions to supersaturate, equilibrium gas samples could be withdrawn. The removal of such a sample necessarily terminated that particular experiment. In this way it was possible to account for the transfer of the more volatile constituents between the phases present.

If the assumption was made that the compressibility of the equilibrium gas phase was substantially the same as that of the original gas used (or some function of it), the apparent solubility of the original gas in the original liquid at various temperatures and pressures could be determined by measurements with the equilibrium cell. This assumption would be most nearly valid at lower temperatures, at lower pressures, and with natural gases containing less of the easily condensable constituents. In these complex hydrocarbon mixtures the solubility of the gas in the liquid loses its exact significance, since the process occurring when the two are brought to equilibrium consists of a partial transfer of constituents from each phase to the other.

APPLICATION TO SIMPLE MIXTURES

Simple hydrocarbon systems containing only two or three constituent substances may be studied with more precision, and a more complete picture of their behavior can be obtained. Such studies, therefore, offer an effective method of determining the fundamental behavior of hydrocarbons in mixtures, thus paving the way to more exact studies of the complex mixtures.

In the case of two-component systems, the entire amount of the less volatile component was admitted first to the equilibrium cell by the method best suited to its volatility. The volume of the liquid phase, if any existed, was then measured. The more volatile component was measured into the equilibrium cell in a series of additions, the resulting equilibrium pressure and liquid volume being determined after each addition, until the pressure reached the working maximum of the apparatus. A series of determinations of this type was made at constant temperature but with systematically varied amounts of the less volatile component initially added. The work was then repeated at different temperatures. It was impossible to obtain precise data in the condensed portions of the system at compositions approaching that of the less volatile component, as the cell was completely full of liquid and the attainment of equilibrium doubtful. The relations between composition, temperature, and pressure for the saturated gas were determined by use of the dew point apparatus. From these data and those from the equilibrium cell, the composition and density of the liquid phase and the density of the gas phase were obtained. The density and compressibility when only one phase was present were determined from the equilibrium cell measurements.

ACKNOWLEDGMENT

Financial assistance in the development of the apparatus and methods described has been received partly from a fund made available to the American Petroleum Institute by John D. Rockefeller and the Universal Oil Products Company and partly from the American Petroleum Institute.

Members of the Fred C. Henson Company, instrument makers, have shown the authors many helpful courtesies during the design and construction of the apparatus. Charles D. Kircher, Jr., and Jan G. Schaafsma have assisted in the installation and testing of the equipment.

RECEIVED August 25, 1933. The data presented in this paper represent work done under Research Project 37 of the American Petroleum Institute.

PRINTED IN U. S. A.

PHASE EQUILIBRIA IN HYDROCARBON SYSTEMS
METHODS AND APPARATUS

* * *

MEASUREMENT OF VISCOSITIES OF LIQUIDS SATURATED WITH GASES AT HIGH PRESSURES

Reprinted from Analytical Edition
INDUSTRIAL AND ENGINEERING CHEMISTRY
Vol. 5, Page 261, July 15, 1933

Measurement of Viscosities of Liquids Saturated with Gases at High Pressures

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THE interest of the petroleum industry in increasing the yield of crude oil from producing formations has caused much thought to be given to the factors controlling its recovery. One of the most important of these appears to be the properties of the oil itself. Previous investigators found that dissolving natural gas in crude oil had a surprising effect on many of its physical properties. A general study of these changes was undertaken at the California Institute as Research Project 37 of the American Petroleum Institute. This paper describes the viscometer developed for the study of the effect of dissolved gas on the viscosity of crude oils.

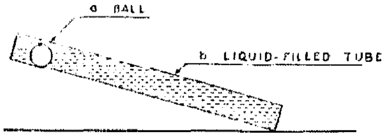

FIGURE 1. DIAGRAM OF BALL AND TUBE

INSTRUMENTAL REQUIREMENTS

In order to duplicate in some measure the range of conditions found in petroleum formations, saturation pressures up to 200 atmospheres (2940 pounds per square inch) and temperatures ranging from 20° to 95° C. (70° to 200° F.) must be attained. The work of other investigators (*1*), at lower pressures, indicated that the change in viscosity of the oil would be very large at saturation pressures of 200 atmospheres. An instrument is therefore required which will measure accurately a wide range of viscosities without requiring intermediate alterations or readjustments. There are several other requirements which must be met by an instrument suitable for this study. Some means must be provided for establishing equilibrium between the gas and oil within a reasonable time. The instrument should be of such a nature that its calibration is independent of pressure. There is also need for means of measuring the saturation pressure and of maintaining the temperature of the viscometer constant during a given set of measurements.

Principle Utilized

The instrument which was found to satisfy most nearly the needs of this work was a modified form of the viscometer developed by Flowers (*3*) and Hersey (*4*). The sketch in Figure 1 illustrates the principle of the instrument. The ball *a* is at the upper end of the closed, liquid-filled tube *b*. As the ball moves down the tube (probably by both rolling and sliding), the displaced liquid must flow past it through the space between the ball and the tube. For any given ball with the tube held at a constant angle, the travel time of the ball multiplied by the difference between the density of the ball and that of the liquid is a linear function of the absolute viscosity of the liquid. This linear function breaks down, however, if the rate of movement of the ball is so great that the flow becomes turbulent.

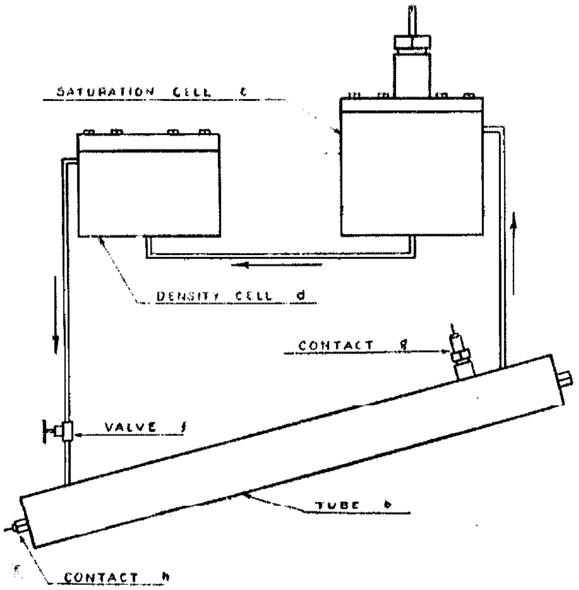

Figure 2. Diagram of Viscosity-Measuring Apparatus

THE INSTRUMENT AND ITS OPERATION

Figure 2 is a sketch of the instrument developed upon the above principle. In order that equilibrium between the gas and oil may be reached, a closed circulating system is provided. The liquid flows from the saturation cell *e* to the density-measuring bomb *d*, thence to the bottom of the inclined tube *b* of the viscometer itself, returning from the top of the tube to the gas space of the saturation cell again. A small cam pump in the bottom of the saturation cell circulates the oil through the system as desired. A photograph of the actual instrument is shown in Figure 3.

The entire system, except the upper part of the saturation cell, is filled with the oil sample, the system being so arranged that any entrapped gas is swept out upon circulation. Liquid is pumped through the system after thermal equilibrium is attained, the ball being forced to the upper end of the tube *b* above the outlet tube. When circulation is stopped, the ball is allowed to move part way down the tube. The upper contact *g* is then screwed down a small amount, and the circulation again started. The ball, moving up the tube, now wedges itself against the lowered contact, and is in position to start a measurement. This procedure of wedging the ball from below the contact gives a sharper and more reproducible release upon raising the contact than is the case with the ball above. The valve *f* at the lower end of the

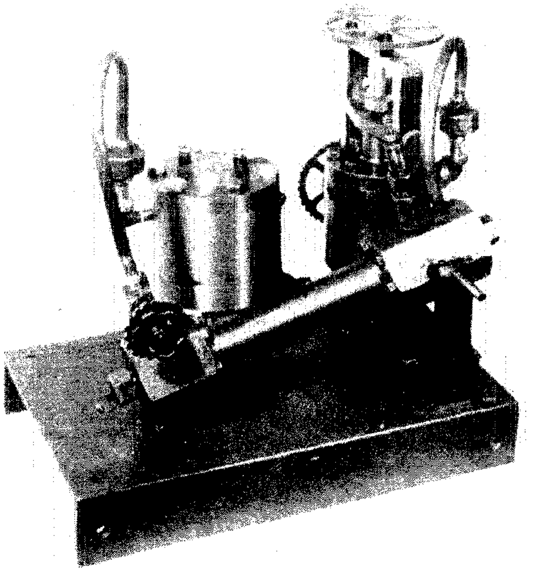

FIGURE 3. PHOTOGRAPH OF INSTRUMENT

ball tube is now closed and the contact lifted, starting the ball down the tube. The break in contact is recorded on a chronograph. When the ball touches the lower contact *h*, another mark is made on the chronograph record. The valve *f* is again opened, circulation reëstablished, and the measurement repeated as often as desired. Next, gas is admitted to the top of the saturation cell and circulation maintained until the attainment of equilibrium is indicated by constancy of pressure reading. A new set of ball times is determined as before, more gas is then admitted, and the measurements are repeated at the resulting higher saturation pressure. This process is continued until the pressure approaches the upper limit of 200 atmospheres (2940 pounds per square inch). A series of determinations of this nature involving measurements at ten different pressures requires in the neighborhood of two hours after the initial thermal equilibrium has been reached.

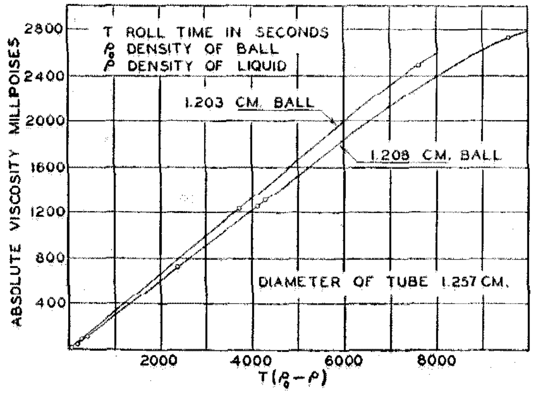

FIGURE 4. CALIBRATION CURVES FOR TWO BALLS

The density of the liquid is measured in the density bomb at each of the saturation pressures by means of a small torsion-mounted balance. Since the two ends of the beam are constructed of materials of different density, the volume displaced is different and the force required to bring the beam into balance is a function of the density of the liquid in which it is immersed. This force is supplied by two solenoid coils, one mounted on the beam, and the other held in a fixed position. When current is passed through the coils a repelling force is exerted between them. By measuring the current flowing through the coils when the beam is in balance, a measure of the density of the liquid in which the beam is immersed is obtained. The instrument is calibrated by immersing it in a series of liquids of known density.

The saturation pressures are measured by means of a fluid pressure scale connected to the gas space of the system through a mercury trap. The trap is necessary to prevent contamination of the gas by the oil used in the fluid pressure scale. The temperature of the viscometer is held at any predetermined value by means of an oil bath controlled by a mercury regulator. The temperature of the bath can be varied between 20° and 95° C. (70° and 200° F.); the maximum variation from the desired temperature during a run is about 0.03° C. (0.05° F.).

CALIBRATION

The viscometer is calibrated by measuring the roll time at atmospheric pressure for liquids of known viscosity. The liquids used in this work were standardized by the Bureau of Standards. The viscosities of these liquids were known at several temperatures, so that the effect of temperature on the calibration of the instrument could be determined.

Figure 4 shows calibration curves for two balls of slightly different sizes. The curves are straight lines over the greater part of the range but flatten off at roll times over twelve to fifteen minutes. This may be due to the break-down of the film between ball and tube. The effect of turbulence can be seen at the short roll times on the upper curve. The instrument gives satisfactory results in this range if enough calibration liquids are used to give the location of the curve with the desired certainty. The marked divergence of the two curves for a small change in ball size points to the need of high accuracy in the machining of both the ball and the tube. It is also evident that change in the surface condition of either the ball or the tube will change the calibration of the instrument to a marked extent. The balls used in this work were spherical to within 0.0001 inch, this degree of accuracy being necessary to obtain duplication of roll times of 0.25 per cent.

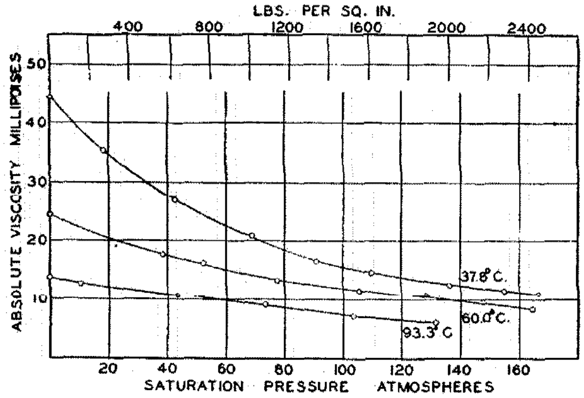

FIGURE 5. VISCOSITY CURVES AT DIFFERENT TEMPERATURES

The effect of pressure on the calibration of the instrument was investigated by comparing the small measured increase in viscosity of water under pressure with that expected from the work of Bridgman (*2*). This comparison indicated that at 170 atmospheres (2500 pounds per square inch) any change in calibration due to pressure could be neglected.

The range of measurable viscosities covered with one ball is quite large, from about 2500 millipoises down to 10 millipoises. However, the long roll times encountered at the higher viscosities make a smaller ball desirable when working in this range.

From the measured roll time and the density of the liquid, it is a simple matter to read the absolute viscosity from the calibration curve. The kinematic viscosity can then be computed from the absolute viscosity and the density.

An illustrative set of results is shown in Figure 5. These viscosity curves are for a sample of Santa Fe Springs oil and dry natural gas at three temperatures. The decreased effect of the dissolved gas at the higher temperatures is probably due to the lower solubility of the gas under these conditions.

CONCLUSIONS

The use of this instrument has indicated that:

1. The viscometer described may be satisfactorily applied to the study of the effect of dissolved gas upon the viscosity of crude oil at relatively high pressures.
2. The instrument is satisfactory for use at temperatures up to 100° C. (212° F.).
3. A wide range of viscosities can be measured with one ball, and to extend such range greatly, only a simple change of ball sizes is needed.
4. Both the ball and the tube must be made with a high degree of accuracy.
5. The density of the liquid must also be measured in order to arrive at either the kinematic or the absolute viscosity.

ACKNOWLEDGMENT

This instrument was developed as part of Research Project 37 of the American Petroleum Institute. Financial support for this work has been received from a fund given jointly by John D. Rockefeller and the Universal Oil Products Company. Credit is due W. N. Lacey for his suggestions and interest in the design of the instrument. Charles Kircher did much to aid in the construction and the operation of the instrument. Acknowledgment is made to Harvey T. Kennedy, of the Gulf Research and Development Corporation, Pittsburgh, Pa., for his suggestion of an improved method of plotting calibration curves.

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RECEIVED March 14, 1933.

PRINTED IN U. S. A.

THE DETERMINATION OF THE THERMAL PROPERTIES
AND THE
PRESSURE-VOLUME-TEMPERATURE RELATIONS OF HYDROCARBON SYSTEMS

THE DETERMINATION OF THE THERMAL PROPERTIES AND THE PRESSURE-VOLUME-TEMPERATURE RELATIONS OF HYDROCARBON SYSTEMS

A knowledge of the thermal properties and the pressure-volume-temperature relations for natural hydrocarbon systems is of interest to the petroleum producer in order to ascertain the available reservoir energy and the most suitable method of employing it in production. Such data on both simple and natural systems are of value in determining the energy relations in subsequent processes where no chemical changes are involved. The methods described in this paper permit the determination of all of the general thermodynamic properties of a hydrocarbon system of constant composition, no matter how complex. The apparatus used has a range from 50°F to 250°F and pressures up to 3000 pounds per square inch.

General Method: The changes in all of the thermal properties at constant temperature are completely determined by the pressure-volume-temperature relations of the system, and can be rigorously calculated from them by application of the fundamental equations of thermodynamic equilibrium.(1) However, the change in at least one thermal property under known conditions (i.e., at a constant pressure or a constant volume) as a function of temperature must be directly measured before all of the thermal properties of the system can be correlated as a function of temperature. The following discussion will deal first, with an apparatus for determination of the pressure-volume-temperature relations, second, with an indirect method of measurement of the specific heat at constant pressure in the condensed region, third, with an adiabatic Calorimeter for measurement of the specific heat at constant volume, and, finally, with the thermodynamic calculations.

The Pressure-Volume-Temperature Apparatus.

The apparatus used in pressure-volume-temperature studies previously described by the author and his co-workers (see part I of this thesis) is not entirely suited for securing data for thermodynamic calculations. It was primarily a constant-volume apparatus in which the change in pressure with composition was followed at constant temperature. The thermodynamic calculations herein described must be made on a system of fixed composition and data obtained with the constant-volume apparatus required much interpolation before it could be used for such calculations. Moreover, this apparatus did not permit extended studies in the condensed region. For these reasons new methods were adopted in order to overcome these difficulties.

A sketch of the apparatus used is shown in Fig. 1. It consists of a steel pressure cell (A) whose inside diameter is two inches and whose height is eleven inches. The volume of this cell may be varied at will by the addition or withdrawal of mercury through a valve located at (B) near the bottom of the cell. The mercury is supplied to the apparatus from a steam-driven reciprocating pump at pressures up to 3500 pounds per square inch. The mercury, before being admitted to the cell, is preheated to the temperature of the apparatus. The volume of the space above the surface of the mercury is determined from the position of the mercury surface. The latter is ascertained by means of an electrical contact (E) which is mounted upon a hollow rod which enters the bottom of the cell through a packing gland. The wire from the electrical contact (E) is brought out of the cell through the hollow rod and is connected through a sensitive relay to a signal light. The lower portion of the rod (C) engages a nut (D) which is in turn driven by the worm (F). A small motor attached to (F) permits the contact (E) to be moved up or down the length of the cell (A). The final adjustment of the position of the contact (E) is made by manual movement of the worm (F). As the rod (C) was threaded with extreme care a counter mounted upon the work (F) gives a direct indication of the position of the mercury surface. A photograph of the exterior of the apparatus is shown in Fig. 2. The total volume over the mercury surface for a given counter reading is determined by adding a known volume of liquid to the cell and determining the counter reading when the cell is just full of liquid at atmospheric pressure. This is indicated by a very rapid rise in pressure for a small addition of mercury. In Fig. 3 is shown a sample calibration curve. The line is extrapolated to atmospheric pressure and permits the determination of the counter reading for a known volume of the cell. The extrapolation to atmospheric pressure is necessary because the density of the calibrating oil is known only at this pressure. Since the cell was carefully machined and the screw was made with high precision (maximum deviation 0.0004 inch in a length of eleven inches) the volume of the cell for any other counter reading could be readily computed. It was found that the position of the mercury surface could be determined within 0.0004 inch which corresponds to a volume of 0.0012 cubic inches (0.02 ml.).

The pressure existing in the cell was measured by means of calibrated fluid pressure scales. One scale having a range from atmospheric to 3000 pounds per square inch and the other a range from atmospheric to 300 pounds per square inch. The reproducible accuracy of each is 1.0 and 0.10 pound per square inch, respectively. They are connected to the bottom of the cell by means of a mercury oil trap.

The temperature of the cell is controlled by an electric heater wound directly on the outside of the cell. In order to maintain constant temperature, a mercury regulator (G) was built directly into the wall of the cell. This regulator is connected through a relay to the heater. An auxiliary heater is provided in the insulated top to prevent possible temperature variation. A cooling coil wound on the cell permits studies below room temperature. The cell is insulated from its surroundings by a one and one-half inch layer of magnesia insulation. Great care was taken in the construction of the heater and in the application of the insulation to insure constant temperature at all points in the inside of the cell. The temperature of the cell is determined by a calibrated thermometer placed in a deep well in the wall of the cell. The uniformity of the temperature throughout the cell was ascertained by the consistency of the dew point of a pure substance at various total volumes of the apparatus. It is believed that the maximum temperature variation throughout the interior of the cell is about 0.2°F. However, as most of the work is done in a restricted region near the top of the cell this small variation is not often encountered.

To secure equilibrium the contents of the cell are agitated by a cage of four vertical rods (H) (see Fig. 1), which is rotated at about 120 revolutions per minute by the shaft (K). This shaft is connected to the cage by a pair of bevel gears not shown in Fig. 1. The addition of this agitator did not affect the uniformity of change in volume of the cell with variation in the height of mercury, as the rods are of uniform diameter and the volume of the ring at the top of the rods is taken into account in the calibration.

The top of the cell is removable to allow the addition of non-volatile liquids. Volatile pure liquids may be distilled into the cell from weighed pressure containers through valve (M). Measured volumes of gas may be admitted through valve (N), which is connected to the rest of the apparatus (see part I of this thesis).

The effect of pressure upon the calibration of the apparatus was determined by maintaining the mercury surface at a fixed position as indicated by a fixed electrical contact in the top of the cell (not shown in Fig. 1) and noting the change in counter reading as the gas pressure over the surface of the mercury was increased from atmospheric to 3000 pounds per square inch. It was found that the maximum pressure correction was less than 0.05 percent at the minimum volume of the apparatus. The effect of temperature upon the calibration of the apparatus was eliminated by calibration at a series of temperatures. The magnitude of this variation of volume due to change in temperature is shown in Fig. 4, which shows the volume of the cell as a function of temperature at the maximum counter reading, which corresponds to the minimum volume of the apparatus.

As an example of the type of data obtained with this apparatus, there are shown in Fig. 5 four isotherms. One is for Kettleman Hills crude oil of the following characteristics. Specific gravity at

60°F, 0.8383 (37.1° API). (Specific gravity as used in this paper refers to the ratio of the weight of a unit volume of the material at a given pressure and temperature to the weight of a unit volume of water at its maximum density at atmospheric pressure.) Molecular weight 188 (freezing-point method). Another of the isotherms is for a mixture of this oil and a blended natural gas of the same composition as that obtained from the flowing well. The fractionation analysis of the gas was the following: Methane 77.0%, ethane 11.0%, propane 6.7%, butane 2.4%, isobutane 1.1%, heavier 1.8%. The ratio of the gas to the oil was 110.3 cubic feet per barrel, both oil and gas being measured at 60°F and one atmosphere. The sharp break in each curve represents the point at which the system becomes entirely liquid. The greater compressibility of the gas-saturated oil is shown by the relative slopes of the two isotherms in the condensed region. The specific gravity in the two-phase region is that of the system as a whole, a quantity which is required for thermodynamic calculations on systems of constant composition.

An isotherm for a mixture of methane (methane 99.29%, ethane 0.01%, nitrogen 0.7%) and impure pentane (97.5% pentane) is also included in Fig. 5. The more nearly linear relation of pressure to volume in the case of the simple mixture in the two-phase region is quite apparent. An isotherm for propane has been included also. The constancy of the vapor pressure in the two-phase region verifies the constancy of the temperature in the cell and the purity of the propane.

Thermal Measurements

Specific Heat at Constant Pressure. After the variable volume cell had been constructed and was found to yield such satisfacotry P-V-T data in the condensed region, it also furnished an admirable apparatus to determine the specific heats of materials in the condensed region. This was done by measuring the changes in temperature due to adiabatic changes in pressure.

In order to measure the change in temperature, a four junction copper constantan thermocouple was installed on the lower surface of the head of the cell (not shown in Fig. 1). One set of junctions was mounted upon two small bakelite posts (1/8 inch diameter) about 3/4 inch below the head of the cell, while the other junctions were mounted in small glass bulbs (1/16 inch diameter), which were set about 1/8 inch in the wall of the steel head. The adiabatic change in pressure was accomplished by connecting the mercury in the cell to an air chamber of sufficient size that the pressure in the tube remained constant in spite of the slight leakage past the plunger of the connected fluid-pressure scale. Another air chamber was provided which was maintained at a somewhat different pressure than the first. The pressure in the tube could then be changed easily and rapidly by closing the valve to the first air chamber and opening that to the second. The change in pressure being directly measured on the fluid-pressure scale. A high sensitivity, low resistance galvanometer in connection with a calibrated potentiometer was used to measure the temperature change due to the adiabatic change in pressure. As the walls remained at substantially the same temperature the cooling curve method had to be employed in order to arrive at the true temperature change. After a little experience it was found possible to commence recording temperatures about ten seconds after the pressure changed. A chronograph was used to record the elapse of time. The record of the change in temperature as a function of time was continued for about one hundred and twenty seconds. In the case of hydrocarbons more viscous than kerosene the effect of convection currents was so small that the cooling curve results could be omitted, for the maximum temperature reached by the liquid could easily be measured before a fall in temperature due to diffusion took place. The value of the thermocouple voltage at zero time yielded, from calibration of the thermocouple, the change in temperature of the liquid for a known change in pressure. From this data a mean value of the $(\frac{\partial T}{\partial p})_s$* could be obtained for the average pressure existing. This measurement was then repeated at a lower pressure and another value of the coefficient obtained. By combining this data with the thermal expansion, $(\frac{\partial v}{\partial T})_p$, according to the general relation $c_p = \frac{T(\frac{\partial v}{\partial T})_p}{(\frac{\partial T}{\partial p})_s}$ the value of the specific heat at constant pressure was obtained.

Specific Heat at Constant Volume. The method for determination of the specific heat at constant pressure is limited to material which may be obtained in the condensed state over the entire temperature range investigated at pressures somewhat below 3000 pounds per square inch. Many natural hydrocarbon systems exist in the two-phase region only at

* For list of symbols used see page 28

pressures well above this value, so the method of adiabatic cooling cannot be applied to them. As measurement of the specific heat must, in such cases, be done in the two-phase region, a constant volume calorimeter offers the simplest method of approach.

The apparatus used for the measurement of the specific heat at constant volume is shown in Fig. 6. It consists of a steel bomb (A) containing the sample, a heater and a thermocouple. The bomb (A) is mounted in a bakelite ring (B) which can be oscillated through about 150 degrees on shaft (K). This motion provides the necessary agitation to insure both thermal and phase equilibrium. The motion is imparted to the shaft (K) by means of cords attached to the grooved pulley (C). In order to insure as little heat interchange between the bomb and its surroundings as possible, an adiabatic jacket (E) made of 1/4 inch copper was provided. In order to maintain the inside of the adiabatic jacket at the same temperature as the exterior surface of the bomb, a thermocouple was provided, one junction being attached to each surface. These were directly connected to a high sensitivity, low resistance galvanometer, which controlled an photoelectric relay. The relay in turn controlled the flow of current through the heater mounted on the outside of the copper jacket (E). Cooling coils were also provided on the outside of the jacket to permit studies below room temperature. A picture of the jacket and accompanying parts of the calorimeter before assembly is shown in Fig. 7. To prevent excessive heat loss from the jacket, it was surrounded by a one-inch layer of diatomaceous earth. The entire calorimeter was placed in the air thermostat which could be maintained at the average temperature of the determination. This prevented any change in the temperature distribution in the jacket when studies are made at different temperatures. In order to further reduce the heat loss or gain by the bomb, a very thin radiation shield (D) was provided. Due to the bakelite ring (B) the metal shaft (K) did not come in contact with the bomb, thus reducing heat exchange from this source. The entire inside of the calorimeter was nickel-plated, covered with a very thin layer of chromium and polished. A picture of the inside of the assembled calorimeter is shown in Fig. 9.

In Fig. 8 are shown the details of the constant-volume bomb, which was built of alloy steel to withstand a maximum working pressure of 3000 pounds per square inch. It consists of a cylindrical steel tube (A) to which the removable heads (B) and (C) are fastened by means of the large hexagonal union nuts (T). The energy is supplied to the interior of the bomb by a non-inductive heater (D) whose leads are brought out at the contacts (E) and (F) located in the head (B). The temperature of the bomb was measured by the thermocouple (G). The leads from this couple were brought through the hollow contacts in the lower head. This avoided any contact voltages at the surface of the bomb. A photograph of the parts of the bomb is shown in Fig. 10. Liquid materials are added by removing one of the heads. Gaseous material is added through the needle valve (H). (see Figure 8) The weight of material added is determined in each case by the difference in the initial and final weight of the bomb. When a mixture is to be studied, each component is added successively, the bomb being weighed after each addition. The amount of energy added to the bomb and contents was determined by the current flow through, and the voltage drop across, the heater (H). These were measured by means of a standard resistance, a volt box, and a potentiometer.

In order to determine the heat capacity of the bomb itself it was almost filled with a non-volatile liquid and placed in the calorimeter. After the jacket had come to temperature and the bomb no longer changed temperature with time, showing that the heat interchange was exceedingly small, the internal heater was turned on for a short period, usually about ten minutes. The bomb was agitated for one minute and allowed to come to equilibrium. The rise in temperature was then measured by connecting the thermocouple junction inside the bomb to another mounted in a well heat-insulated copper block which was brought to the temperature of the air thermostat and did not change with time. By this means the range of the potentiometer could be reduced so as to just cover the rise in temperature of the bomb and permitted much more accurate measurement of the temperature rise. The measurement of the temperature rise due to the addition of a known amount of energy was repeated at a series of temperatures covering the entire range. Another set of similar measurements was then made with the bomb only about one quarter full of liquid and from this data on the heat capacity of the bomb and two different quantities of oil the heat capacity of both the bomb alone and that of the oil could be calculated. The heat capacity of the bomb as a function of temperature is shown in Fig. 11.

It was found that the jacket followed the bomb so closely that the temperature of the bomb remained constant within 0.01°F for several hours after the current in the interior heater had been turned off.

With this in view, no correction for heat loss was needed nor was there any need to use a cooling curve to determine the true temperature rise. The short period of agitation did not add enough energy to warrant a correction, for the energy added in this way only changed the temperature of the bomb about 0.09°F per hour of agitation.

Due to the large heat capacity of the bomb, the specific heat at constant volume is only reproducible to about 1.5%. However, as this requires that the heat capacity of the bomb and contents be known to at least 0.3% it is considered satisfactory.

Thermal Calculations for Hydrocarbon Systems. From the pressure-volume-temperature data and a single measured thermal property as a function of temperature, the calculation of the entire thermal behavior of a system of constant composition is possible. Of the various graphical methods of presentation available, the temperature-entropy plane furnishes the best picture when both the condensed and superheated regions are included. The following discussion will apply to the construction of such a chart including the five variables, pressure, temperature, volume, heat content, and entropy.

As convenient datum conditions, the entropy and the heat content of the saturated liquid are arbitrarily taken as zero at the lower temperature limit of the experimental data. At this lowest temperature the change in entropy with pressure can be calculated by use of the general equilibrium equation $(\frac{\partial s}{\partial p})_T = (\frac{\partial v}{\partial T})_p$. This relation cannot be used in the two-phase region in the case of a pure substance, but can there be replaced by the Clapeyron equation,

$\Delta h = \frac{dp}{dT} T \Delta v$. From the above-mentioned relation of entropy to pressure at constant temperature the position of a series of constant pressure and volume intercepts can be determined at the datum temperature, the pressure-volume-temperature data being directly employed to locate the constant volume lines after the constant pressure lines had been determined. Again this procedure is somewhat modified in the two-phase region of a pure substance. From direct thermal measurement the position of either a constant volume line or a constant pressure line can be determined as a function of temperature by use of the proper one of the two following relations:

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T} \qquad \left(\frac{\partial s}{\partial T}\right)_p = \frac{C_p}{T}$$

As the intersection of this line with the datum temperature is known and its slope determined by the above relations it can be readily drawn on the temperature-entropy plane. From the pressure-volume-temperature data the pressure and the volume is known at each temperature along this line and by applying the same methods as were used at the datum temperature the entire field of constant pressure and volume lines can be drawn in.

The change in heat content with pressure at constant temperature can be determined by graphical integration of the expression

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p$$

By following the same method as outlined above a field of constant pressure lines may be drawn on the heat content-temperature plane. There is no need of including the constant volume lines on this auxiliary plane as they are already fixed on the temperature-entropy plane. The relation $\left(\frac{\partial h}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_p = C_p$ is used to establish one constant pressure line as a function of temperature from the directly measured thermal quantities. From the temperature-heat content plane the temperatures at which constant heat lines intersect constant pressure lines can be determined and the constant heat content lines transferred to the temperature-entropy plane.

All of the above calculations can be done by mathematical analysis but the author feels that the graphical methods employed do much to correlate the data and to point out errors. Tabulated data are taken from the final charts which were drawn to a scale to make the tabulation accurate to at least 0.5% throughout the entire range. Work of this nature on many hydrocarbon systems would require for practical application only a small part of the range usually covered in the thermal studies of pure substances. In general, data would only be needed for the condensed region and a part of the two-phase region for a normal crude oil-natural gas mixture. In production practice, one would never reach pressures low enough to encounter the saturated gas line nor would production operations go to temperatures high enough to reach the critical temperature of the mixture. Again, on the other side of the composition scale with a wet natural gas, one would need to cover most of the superheated region and the saturated gas relations but would only be required to go a little way into the two-phase region as temperatures ordinarily met are above the critical temperature of the gas and below the cricondentherm, (i.e., the maximum temperature at which two phases can exist). However, the pressure might be far below that necessary to reach a one-phase region. In the case of a very dry gas, temperatures would probably be above the cricondentherm and one would ordinarily never encounter any two-phase region at all.

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SYMBOLS USED

C_p	Specific heat at constant pressure expressed as the ratio of the heat required to raise a mass of material 1°F at a constant pressure to that required to raise an equal mass of water 1°F at its maximum density under a total constant pressure of 1 atmosphere.
T	Absolute temperature in degrees Rankine.
v	Volume occupied by a unit mass of material expressed as cubic feet per pound.
p	Absolute total equilibrium pressure exerted on the system by its surroundings, expressed in pounds per square inch.
s	Specific entropy expressed in Btu per pound per degree Rankine.
h	Specific heat content expressed in Btu per pound.

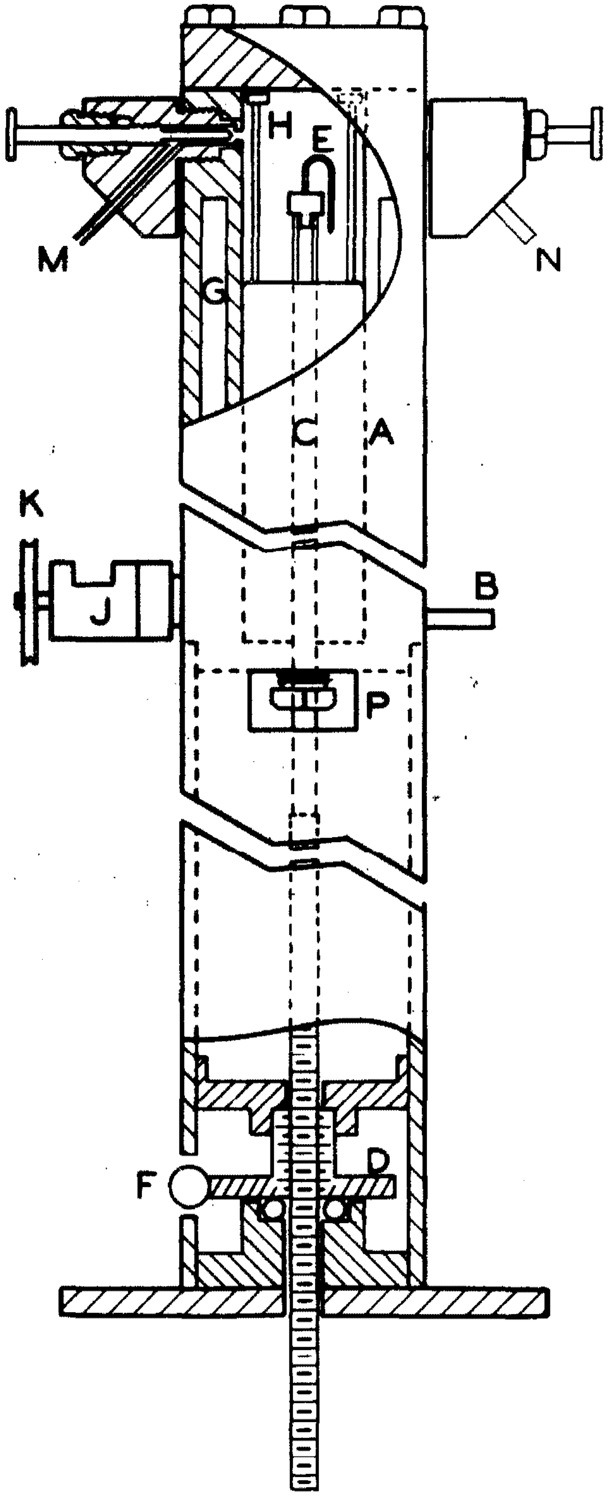

Fig. 1

Variable Volume Apparatus

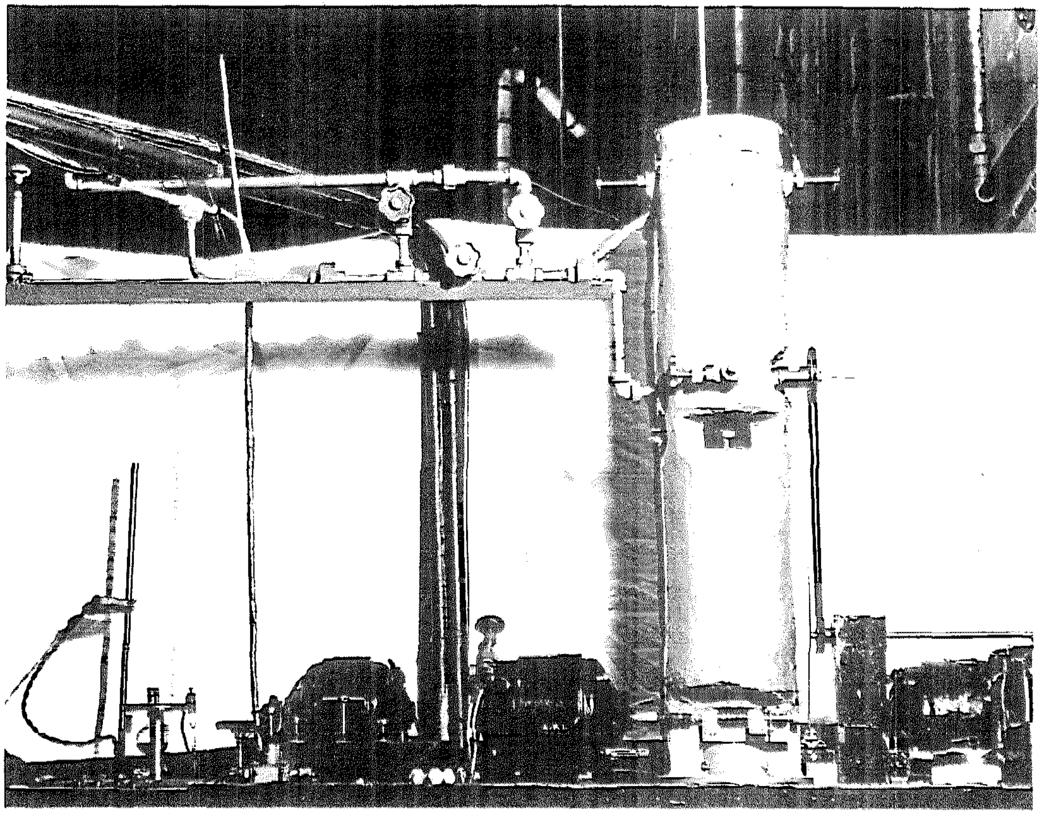

Fig. 2
General Arrangement of Variable Volume Apparatus

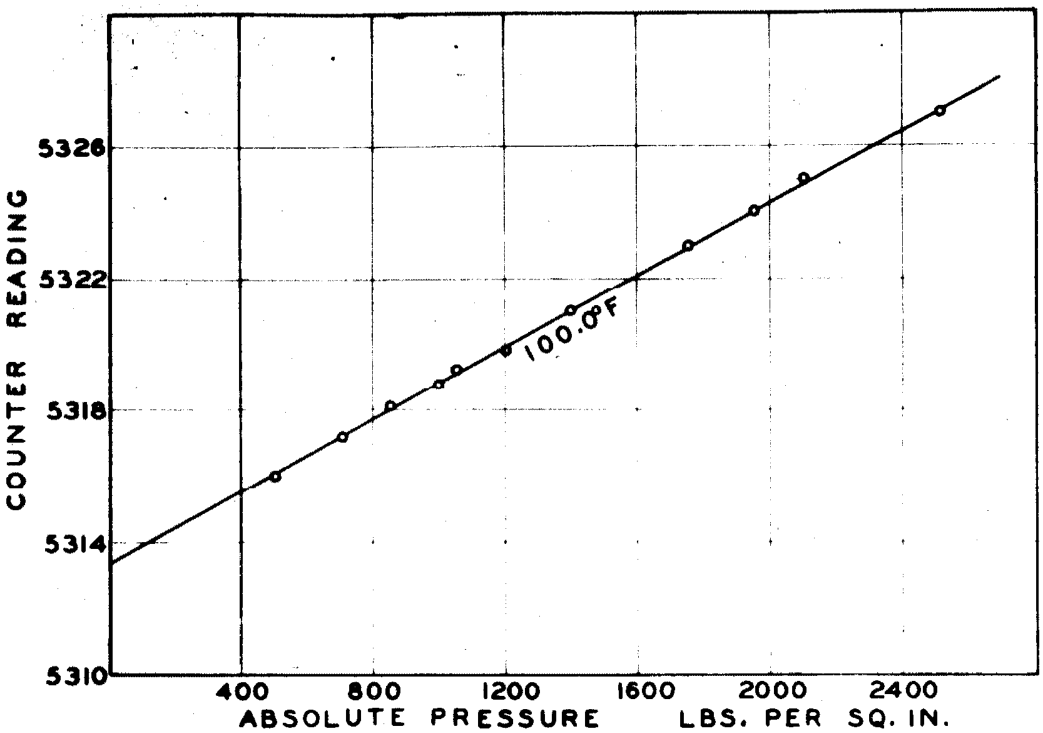

Fig. 3

Sample Calibration

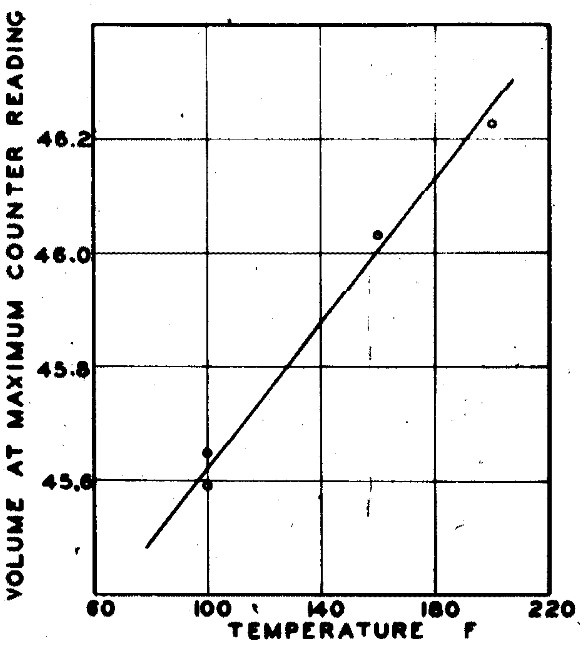

Fig. 4

Temperature Correction

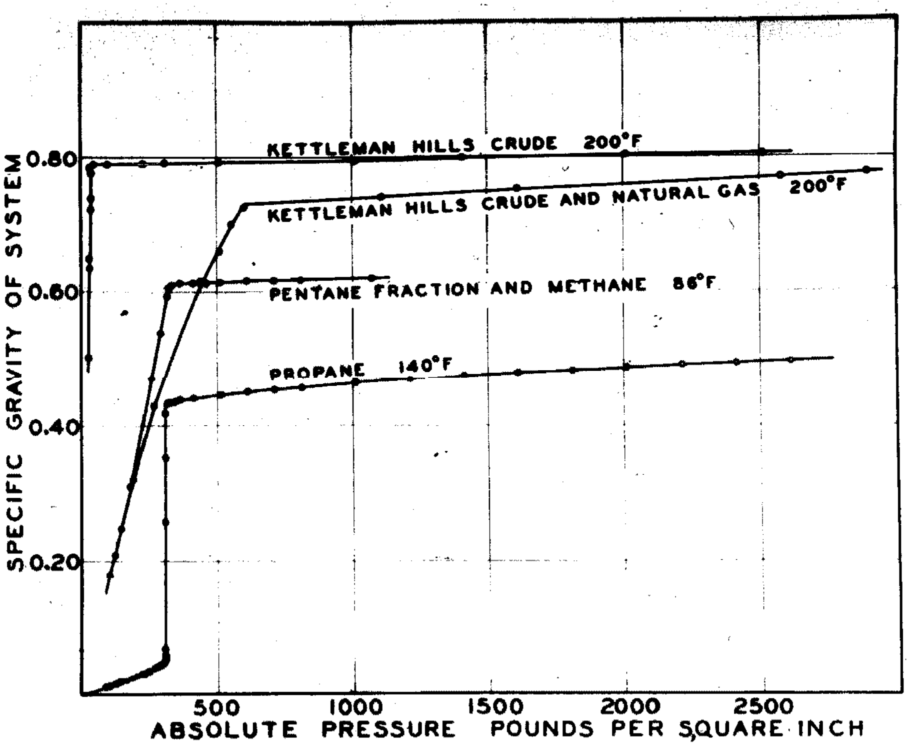

Fig. 5

Sample Isotherms

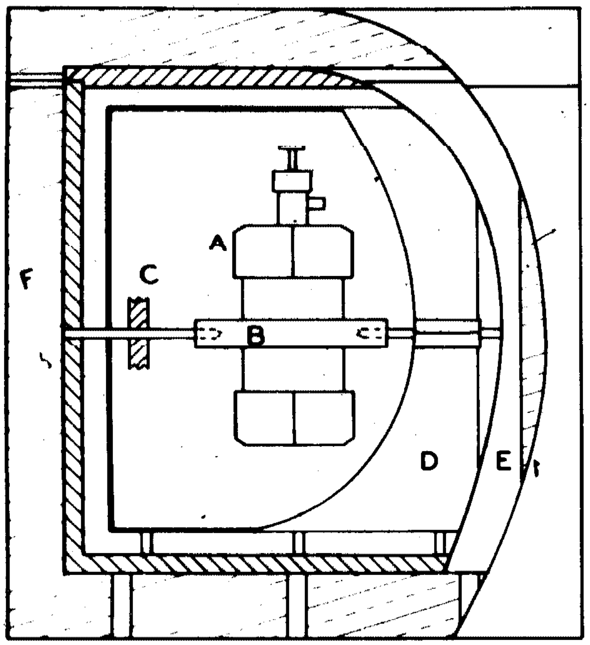

Fig. 6

Constant Volume Adiabatic Calorimeter

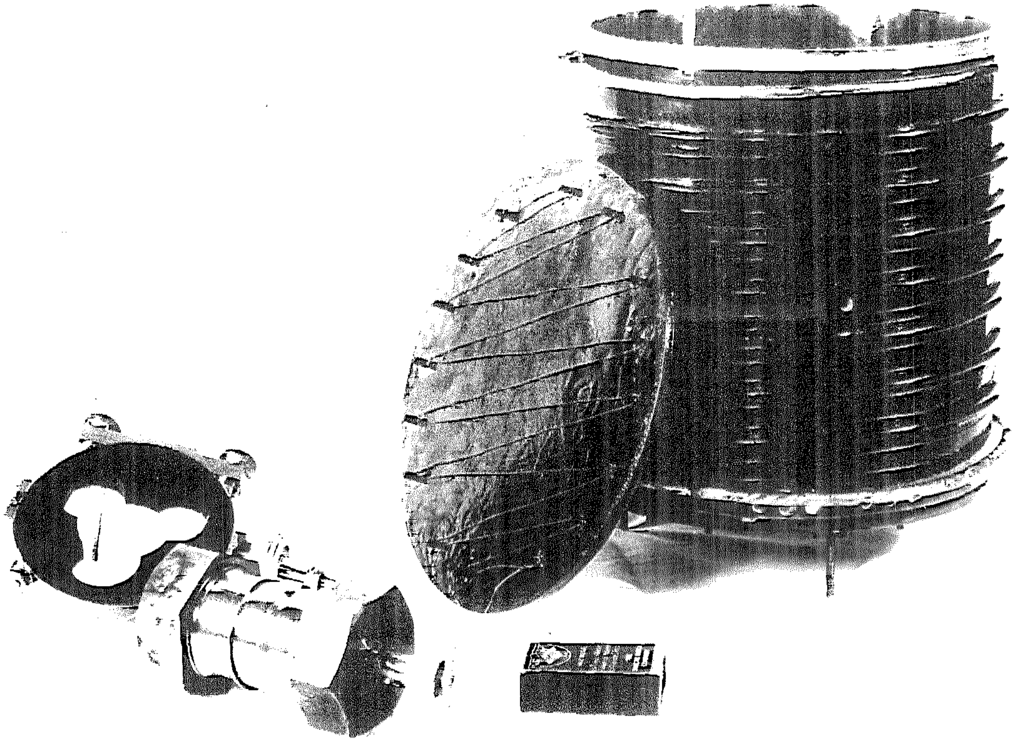

Fig. 7
Unassembled Calorimeter

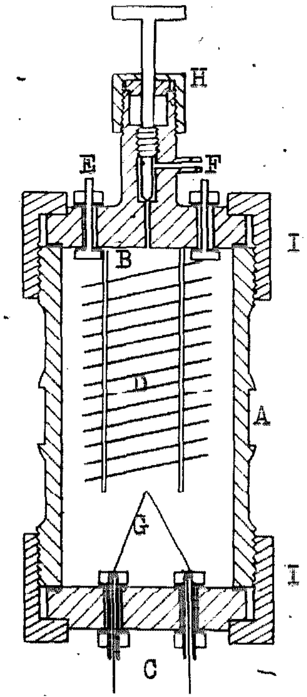

Fig. 8
Section of Calorimeter Bomb

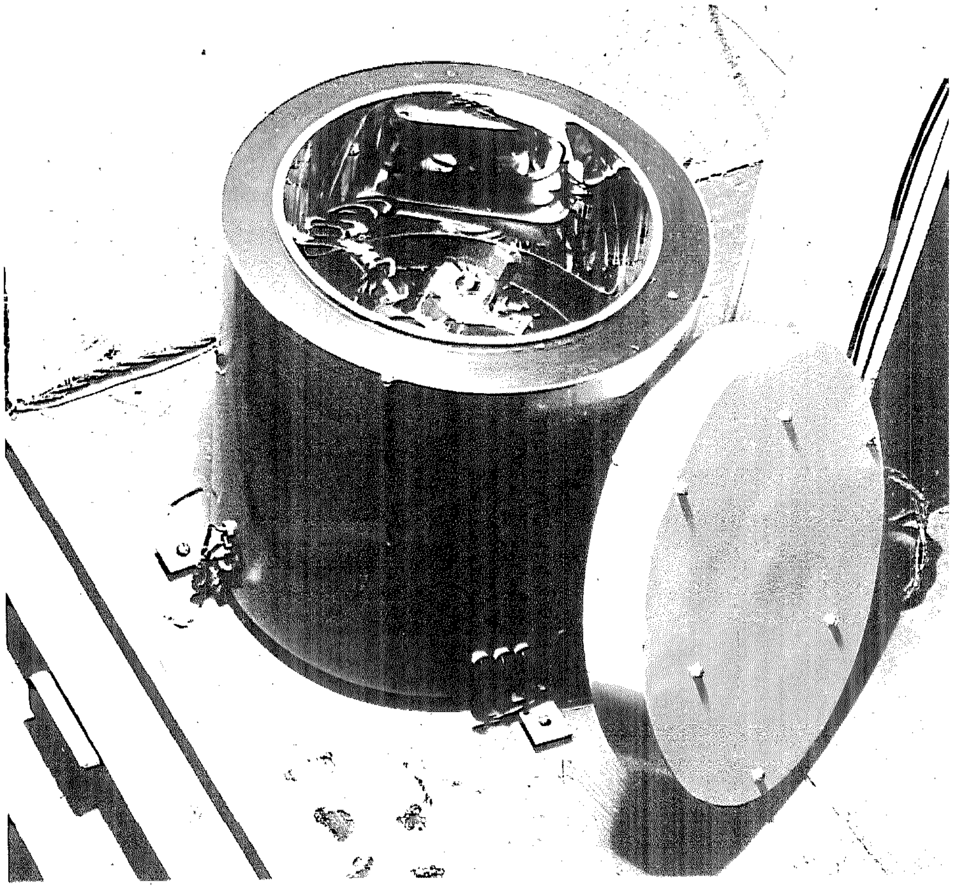

Fig. 9
Assembled Calorimeter

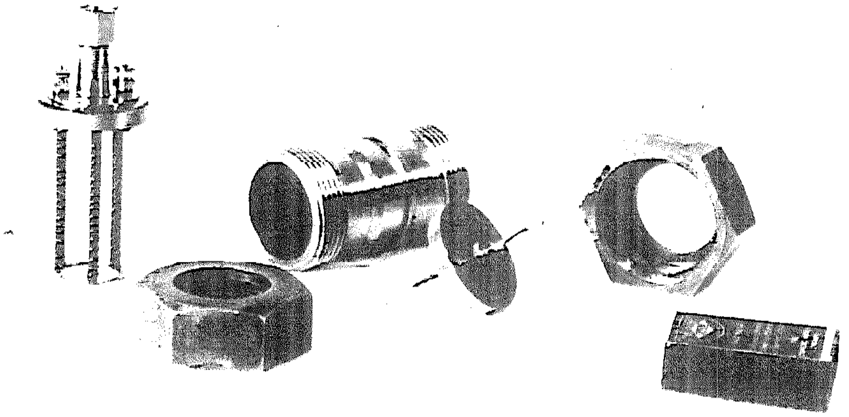

Fig. 10

Parts of Calorimeter Bomb

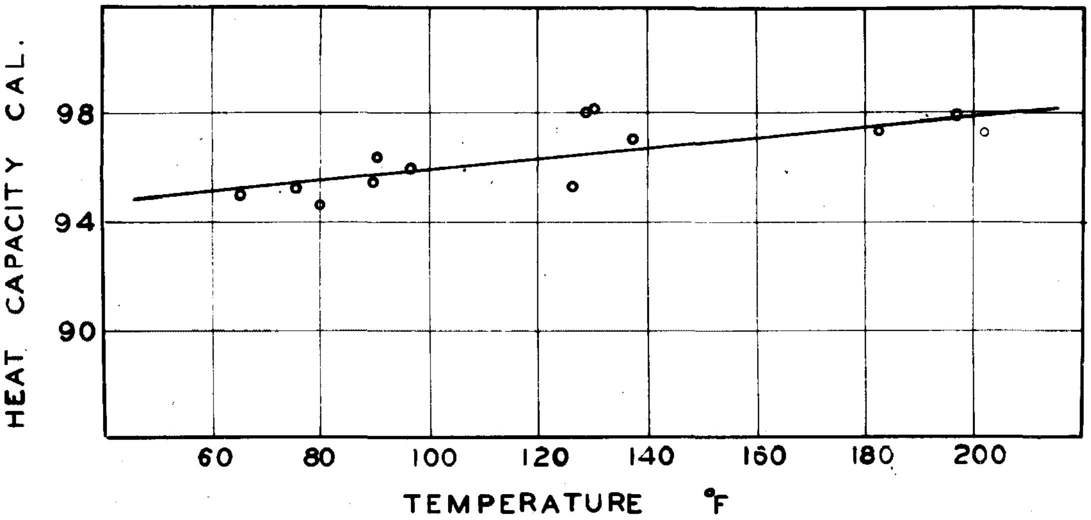

Fig 11

Heat Capacity of Calorimeter

Reprinted from
INDUSTRIAL AND ENGINEERING CHEMISTRY
Vol. 26, Page 214, February, 1934

Phase Equilibria in Hydrocarbon Systems

II. Methane-Propane System

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The methane-propane system is studied throughout the temperature and pressure ranges commonly found in underground petroleum formations. This system may be considered as illustrating the behavior of a simplified case of natural gas in contact with very high-gravity volatile oil. Complete equilibrium data are accompanied by illustrative diagrams prepared therefrom.

IN STUDIES of the equilibrium behavior of systems consisting of hydrocarbons, such as the mixtures of petroleum and natural gas found in nature, the investigator is faced with a problem of great complexity. It would seem desirable, therefore, to approach the problem by establishing first the behavior of some simpler hydrocarbon systems under similar conditions of temperature and pressure. By choosing a two-component system, a complete record of equilibrium data may be obtained for the desired range of conditions at the expense of a small fraction of the time required to reach even a partial solution of the very complex case.

The results of such a study of the methane-propane system are here reported. The pressures and temperatures were restricted to those generally found in petroleum formations—i. e., 1 to 200 atmospheres and 20° to 90° C. The compositions were varied continuously from pure propane to pure methane. Measurements of density and composition were made in both the one- and two-phase regions, including a large region above the critical pressures of the system.

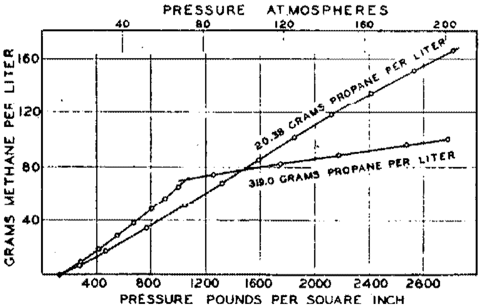

FIGURE 1. TYPICAL EXPERIMENTAL CURVES FROM EQUILIBRIUM CELL

EXPERIMENTAL METHOD

A detailed description of the apparatus used and methods employed for a two-component system is given in Part I of this series (*6*). In brief the method consisted of the following steps: The pressure-composition relations of saturated gas[1] were determined by dew point measurements at a series of temperatures. Eight or ten different compositions were employed at each temperature. Dew points were obtained for both normal and retrograde condensation.

The total density and composition were determined by measuring the increase in equilibrium pressure due to the addition of successive known quantities of methane to an equilibrium cell containing a known amount of propane. By a series of seven or eight sets of measurements of this nature at systematically chosen concentrations of propane (expressed as grams per liter of total space), the entire field of compositions could be mapped for the chosen temperature. For illustration, two such sets of measurements made at 21.1 C. (70° F.) are shown in Figure 1. In the case of the curve with the lower concentration of propane there was very little liquid phase in the equilibrium cell and this rapidly disappeared. In the other case the cell was over half full of liquid at the beginning of the addition of methane, and the volume of the liquid phase increased until the cell was completely full at the break in the curve. This point represents the pressure of saturated liquid of the composition corresponding to the total composition of the mixture at this point. The locus of these break points for different sets of measurements gave the relations of pressure, density, and composition for saturated liquid. The volume of the liquid phase was also measured after each addition of methane to furnish a check on the boundary measurements. These measurements were carried on at five temperatures evenly distributed

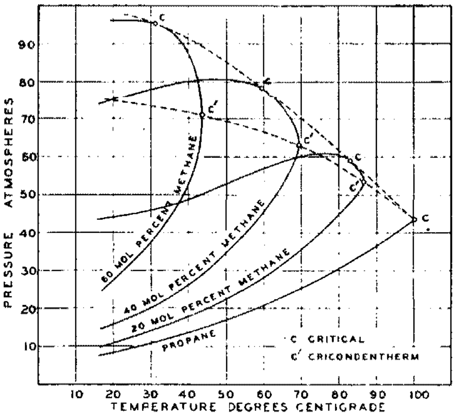

FIGURE 2. CONSTANT COMPOSITION CURVES ON PRESSURE *vs.* TEMPERATURE DIAGRAM

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[1] The term "saturated gas" is used here to designate the gaseous phase in equilibrium with a corresponding liquid phase. The latter phase is referred to as the saturated liquid.

Table I. Densities of Mixtures of Methane and Propane

(Compositions expressed in mole per cent methane, densities in grams per liter)

Pressure	20.0 Mole %		30.0 Mole %		40.0 Mole %		50.0 Mole %		60.0 Mole %		70.0 Mole %		80.0 Mole %		90.0 Mole %	
Atm.	Density	State	Density	State	Density	State	Density	State	Density	State	Density	State	Density	State	Density	State
TEMPERATURE, 20° C.																
10.0	18.0	G	16.3	G	14.8	G	13.3	G	11.8	G	10.4	G	9.2	G	8.0	G
20.0	107.8	L + G	61.4	L + G	41.1	L + G	29.4	L + G	24.2	G	21.1	G	19.0	G	16.3	G
30.0	245.5	L + G	126.9	L + G	84.9	L + G	59.7	L + G	44.0	L + G	35.0	G	29.5	G	24.6	G
40.0	381.4	L + G	213.7	L + G	135.4	L + G	92.7	L + G	67.3	L + G	50.9	G	41.4	G	33.8	G
50.0	...	..	308.5	L + G	193.1	L + G	130.8	L + G	93.7	L + G	70.1	R	54.8	G	43.9	G
60.0	...	..	421.8	L + G	260.1	L + G	174.3	L + G	123.3	L + G	91.5	R	69.7	G	55.0	G
70.0	...	..	...	..	339.3	L + G	221.8	L + G	156.1	L + G	113.8	R	85.6	G	66.2	G
80.0	...	..	...	..	385.0	L	279.5	L + G	195.0	L + G	138.2	R	102.3	G	78.2	G
90.0	...	..	...	..	393.5	L	333.6	L	239.2	L + G	167.2	R	119.6	G	90.3	G
100.0	...	..	...	..	400.1	L	345.5	L	276.2	L	196.1	G	138.0	G	102.1	G
120.0	...	..	...	..	410.5	L	366.0	L	306.0	L	235.7	G	172.8	G	127.5	G
140.0	...	..	...	..	418.8	L	380.0	L	327.8	L	265.6	G	203.0	G	147.4	G
160.0	...	..	...	..	425.7	L	391.1	L	344.0	L	286.9	G	227.1	G	172.9	G
180.0	...	..	...	..	432.8	L	401.3	L	357.1	L	304.0	G	247.9	G	193.0	G
200.0	...	..	...	..	438.8	L	410.0	L	367.7	L	317.4	G	265.5	G	210.9	G
TEMPERATURE, 40° C.																
10.0	16.8	G	15.2	G	13.9	G	12.6	G	11.3	G	10.0	G	8.6	G	7.6	G
20.0	47.1	L + G	34.2	G	31.7	G	26.0	G	23.2	G	20.0	G	17.7	G	15.1	G
30.0	152.1	L + G	83.9	L + G	58.6	L + G	44.0	G	37.6	G	31.2	G	26.3	G	22.8	G
40.0	270.8	L + G	146.9	L + G	97.7	L + G	70.1	L + G	55.0	G	44.8	G	37.1	G	31.1	G
50.0	417.8	L	224.6	L + G	141.5	L + G	99.3	L + G	75.4	G	58.7	G	48.4	G	40.0	G
60.0	422.1	L	316.6	L + G	193.0	L + G	133.1	L + G	96.7	R	74.8	G	60.6	G	49.6	G
70.0	427.2	L	384.2	L	255.1	L + G	170.1	L + G	123.1	R	93.3	G	73.6	G	59.4	G
80.0	...	..	393.1	L	326.6	L + G	211.0	L + G	150.0	R	112.7	G	87.0	G	69.0	G
90.0	...	..	400.2	L	347.2	L	264.2	L + G	180.1	G	132.3	G	101.9	G	78.8	G
100.0	...	..	406.1	L	358.8	L	289.5	L	209.7	G	151.6	G	115.9	G	89.1	G
120.0	...	..	416.7	L	376.1	L	317.8	L	249.6	G	188.5	G	144.5	G	110.2	G
140.0	...	..	425.2	L	388.6	L	337.1	L	278.2	G	220.1	G	169.8	G	129.5	G
160.0	...	..	433.3	L	399.4	L	352.5	L	299.2	G	245.0	G	192.8	G	149.8	G
180.0	...	..	440.0	L	407.3	L	365.1	L	316.4	G	263.8	G	213.1	G	167.7	G
200.0	...	..	...		415.1	L	375.4	L	331.0	G	279.8	G	229.2	G	183.7	G
TEMPERATURE, 55° C.																
10.0	16.3	G	14.8	G	13.2	G	12.1	G	10.9	G	9.6	G	8.3	G	7.1	G
20.0	35.2	G	30.3	G	27.5	G	24.5	G	22.0	G	19.4	G	16.7	G	14.3	G
30.0	88.4	L + G	52.0	G	44.9	G	38.8	G	33.8	G	29.6	G	25.5	G	22.0	G
40.0	188.0	L + G	105.2	L + G	67.0	G	56.3	G	47.8	G	40.0	G	35.0	G	29.4	G
50.0	295.6	L + G	166.4	L + G	107.9	L + G	77.9	G	64.0	G	52.7	G	44.4	G	37.2	G
60.0	379.1	L	236.7	L + G	150.6	L + G	105.9	R	82.2	G	66.5	G	54.9	G	45.6	G
70.0	389.9	L	320.3	L + G	198.1	L + G	136.2	R	102.1	G	81.1	G	65.8	G	54.2	G
80.0	397.3	L	345.2	L	252.5	L + G	119.4	G	123.6	G	96.4	G	77.2	G	63.2	G
90.0	403.4	L	359.8	L	284.2	L	202.6	G	145.7	G	111.9	G	89.1	G	71.9	G
100.0	408.4	L	369.7	L	306.3	L	231.7	G	168.3	G	127.5	G	101.4	G	80.8	G
120.0	...	..	384.2	L	336.7	L	274.1	G	211.3	G	159.9	G	125.5	G	98.8	G
140.0	...	..	395.3	L	356.3	L	302.8	G	243.3	G	190.0	G	149.4	G	117.1	G
160.0	...	..	405.3	L	371.8	L	324.1	G	268.4	G	216.9	G	171.2	G	135.2	G
180.0	...	..	414.4	L	383.2	L	338.6	G	288.6	G	237.9	G	191.5	G	152.1	G
200.0	...	..	...	..	392.2	L	351.7	G	304.9	G	256.1	G	208.8	G	166.9	G
TEMPERATURE, 70° C.																
10.0	15.5	G	14.1	G	12.8	G	11.5	G	10.3	G	9.1	G	7.9	G	6.8	G
20.0	33.5	G	29.1	G	26.5	G	23.8	G	21.1	G	18.8	G	16.4	G	13.7	G
30.0	57.9	G	46.8	G	42.0	G	36.5	G	32.3	G	27.7	G	24.9	G	20.4	G
40.0	113.1	L + G	71.5	G	59.2	G	51.0	G	44.8	G	38.0	G	33.4	G	28.0	G
50.0	201.6	L + G	113.6	L + G	82.0	G	67.8	G	57.5	G	48.0	G	42.0	G	35.2	G
60.0	308.5	L + G	173.7	L + G	113.2	G	87.3	G	71.2	G	60.3	G	50.9	G	42.7	G
70.0	339.8	L	239.5	L	153.9	G	109.9	G	87.5	G	72.2	G	60.8	G	50.8	G
80.0	353.9	L	283.8	L	196.4	G	136.7	G	104.4	G	85.1	G	70.9	G	58.8	G
90.0	362.4	L	310.3	L	232.1	G	165.9	G	122.9	G	98.2	G	81.0	G	67.1	G
100.0	368.8	L	327.0	L	260.6	G	193.8	G	143.2	G	112.9	G	92.2	G	75.0	G
120.0	...	..	348.3	L	207.9	G	236.9	G	180.9	G	140.7	G	113.5	G	91.3	G
140.0	...	..	364.3	L	324.1	G	269.4	G	215.3	G	168.9	G	135.4	G	107.9	G
160.0	...	..	...	..	342.9	G	294.8	G	240.9	G	195.6	G	156.4	G	125.1	G
180.0	...	..	...	..	357.6	G	310.9	G	262.5	G	216.4	G	175.9	G	140.9	G
200.0	...	..	...	..	368.6	G	326.8	G	279.6	G	234.9	G	191.0	G	155.1	G
TEMPERATURE, 90° C.																
10.0	14.6	G	13.2	G	12.0	G	10.8	G	9.7	G	8.5	G	7.4	G	6.4	G
20.0	32.9	G	27.8	G	25.1	G	23.0	G	20.2	G	17.1	G	15.7	G	13.1	G
30.0	54.4	G	45.9	G	41.6	G	36.1	G	31.2	G	26.8	G	24.8	G	20.1	G
40.0	81.7	G	66.0	G	57.0	G	49.0	G	42.3	G	37.0	G	31.8	G	26.8	G
50.0	117.1	G	90.3	G	73.5	G	62.9	G	54.3	G	47.0	G	39.9	G	33.5	G
60.0	169.7	G	118.9	G	93.4	G	78.4	G	66.2	G	56.5	G	47.9	G	40.5	G
70.0	242.2	G	157.8	G	117.4	G	96.3	G	81.0	G	67.8	G	56.9	G	47.3	G
80.0	288.3	G	203.2	G	144.5	G	114.4	G	95.4	G	79.1	G	66.0	G	55.0	G
90.0	313.2	G	238.7	G	175.0	G	134.9	G	111.0	G	91.5	G	74.4	G	62.8	G
100.0	327.7	G	264.8	G	202.9	G	155.8	G	125.3	G	102.9	G	85.0	G	70.1	G
120.0	...	..	304.6	G	245.9	G	195.3	G	155.4	G	127.9	G	105.1	G	85.9	G
140.0	...	..	330.2	G	278.3	G	226.7	G	183.2	G	150.0	G	124.1	G	100.9	G
160.0	...	..	...	..	302.2	G	253.2	G	207.8	G	172.0	G	141.1	G	115.9	G
180.0	...	..	...	..	320.4	G	273.9	G	228.9	G	190.8	G	158.3	G	130.0	G
200.0	...	..	...	..	335.5	G	291.8	G	244.9	G	209.1	G	174.2	G	142.4	G

over the range from 20° to 90° C. As illustrated in the curves of Figure 1, the measurements were carried in each case far beyond the disappearance of the two-phase region.

PREPARATION OF MATERIALS

The methane used for this work was prepared from natural gas. The gas under 20 atmospheres pressure was passed through a trap, immersed in a mixture of solid carbon dioxide and methanol, to remove water and heavy hydrocarbons. The gas was then completely liquefied in a steel bomb immersed in liquid air. The partially filled bomb was pumped down to a pressure of 4 to 6 cm. of mercury for an extended time to remove nitrogen and other noncondensable gases. The methane was then partially separated from the other hydrocarbons by a simple distillation into a cooled (10° C.) steel cell containing activated charcoal. This cell was operated at a pressure of about 34 atmospheres. The methane from the cell was stored in steel cylinders. A combustion and modified condensation analysis gave the following composition for the methane:

	Mole %
Ethane (and heavier)	0.03
Nitrogen	0.5
Methane	99.47

Table II. Compositions and Densities of Saturated Liquid and Saturated Gas Phases

(Compositions in mole per cent methane, densities in grams per liter)

Pressure	At 20° C.				At 40° C.				At 55° C.			
	Composition		Density		Composition		Density		Composition		Density	
	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid
Atm.												
10.0	13.2	0.8	...	...	..	..	...	...	..	..	...	...
15.0	38.6	..	...	...	7.9	0.7	...	...	..	..	...	...
20.0	50.5	6.2	28.8	491.3	27.3	3.5	36.0	461.9	3.7	0.5	41.8	439.2
25.0	57.5	..	...	...	37.9	..	...	...	19.6	..	...	...
30.0	61.9	11.6	40.8	479.1	45.1	9.2	49.1	448.6	29.2	5.5	55.0	425.8
35.0	65.4	..	...	...	50.3	..	...	...	35.5	..	...	...
40.0	68.1	17.6	54.3	464.9	54.2	14.9	61.5	432.3	40.1	10.8	67.7	407.8
45.0	70.1	..	...	...	57.1	..	...	...	43.9	..	...	...
50.0	71.4	23.6	68.5	447.1	59.2	20.8	75.8	413.9	47.0	16.7	82.9	387.6
55.0	..	..	...	...	60.6	..	...	...	..	..	...	...
60.0	72.8	29.8	84.3	424.3	61.5	26.6	93.0	392.0	51.1	22.8	102.1	361.4
65.0	..	..	...	...	..	..	...	...	..	..	...	...
70.0	73.6	36.3	102.2	396.7	62.2	32.9	113.9	366.1	52.4	29.2	127.2	327.8
75.0	..	..	...	...	..	..	...	...	52.1	32.6	...	...
80.0	73.4	43.6	123.8	361.6	62.1	39.5	140.4	332.9	50.1	37.5	172.4	271.4
85.0	..	..	...	...	61.4	43.9	...	...	..	..	...	...
90.0	71.4	52.4	155.2	312.8	59.3	50.6	190.2	268.2	..	..	...	...
95.0	69.0	58.3	...	...	..	..	...	...	..	..	...	...

Pressure	At 70° C.				At 80° C.				At 90° C.			
	Composition		Density		Composition		Density		Composition		Density	
	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid	Gas	Liquid
Atm.												
10.0	..	..	...	...	..	..	...	...	..	..	...	...
15.0	..	..	...	...	..	..	...	...	..	..	...	...
20.0	..	..	...	...	..	..	...	...	..	..	...	...
25.0	..	..	...	...	..	..	...	...	..	..	...	...
30.0	10.3	2.1	64.7	401.4	..	..	...	...	..	..	...	...
35.0	18.9	..	...	...	8.5	2.0	...	...	..	..	...	...
40.0	25.2	7.4	70.0	381.8	14.0	4.6	97.4	361.2	4.4	1.0	127.5	332.2
45.0	29.9	..	...	...	20.2	..	...	...	12.1	3.8	...	...
50.0	33.6	13.0	97.1	354.9	24.3	10.6	118.4	328.1	15.2	6.9	163.6	282.7
55.0	..	..	...	...	27.4	2.8	...	...	..	..	...	...
60.0	38.8	19.9	122.2	318.2	27.3	18.3	171.5	265.2	..	..	...	...
65.0	39.2	24.1	...	...	..	..	...	...	..	..	...	...
70.0	..	..	...	...	..	..	...	...	..	..	...	...
75.0	..	..	...	...	..	..	...	...	..	..	...	...
80.0	..	..	...	...	..	..	...	...	..	..	...	...
85.0	..	..	...	...	..	..	...	...	..	..	...	...
90.0	..	..	...	...	..	..	...	...	..	..	...	...
95.0	..	..	...	...	..	..	...	...	..	..	...	...

Owing to the method of analysis employed, the quantity of nitrogen reported is possibly somewhat larger than that actually present.

The propane used for this work was obtained from the Phillips Petroleum Corporation and was not further purified. The Phillips Petroleum Corporation upon careful analysis, found the sample to be pure propane, containing neither ethane nor isobutane in appreciable amounts.

The purity of the methane was further tested by comparison of its measured densities under various pressures with those calculated from published compressibility factors (*5*). The deviation of the two values was in all cases less than one gram per liter over the entire pressure range (1 to 200 atmospheres). The vapor pressure, as well as the saturated vapor and saturated liquid densities of the propane, agreed within experimental accuracy with published values (*3*).

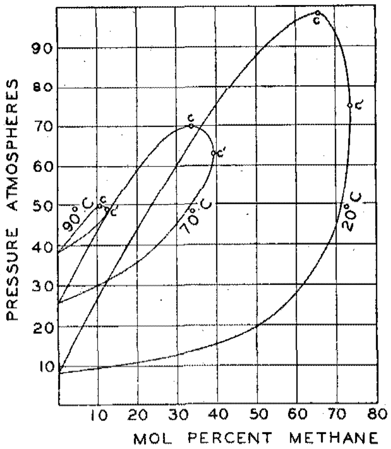

Figure 3. Constant Temperature Curves on Pressure *vs.* Composition Diagram

Accuracy of Measurements

The absolute accuracy of the pressure measurements was 0.10 atmosphere. The temperatures were measured to 0.01° C. and are accurate to at least 0.10° C. The methane and propane were measured to 1.0 ml. (standard conditions) with an estimated absolute accuracy of 0.1 per cent.

Experimental Results

Since the direct experimental data, as typified by the points shown in Figure 1, present the results in a form difficult to tabulate or to use, they have been plotted on as large a scale as is consistent with their accuracy, and the corresponding curves drawn. From these curves points have been read at suitable regular intervals. The data so obtained are reported in the tables. The maximum temperature interpolation was 2.20° C. The absolute accuracy of the tabulated data is: temperature to 0.10° C., pressures to 0.10 atmosphere, compositions to 0.10 mole per cent, and densities to 0.50 gram per liter.

Table I shows the total densities for a series of temperatures, pressures, and total compositions. The state of the system under these specified conditions is also given. L represents liquid only; G, gas phase only; and L + G, coexistence of liquid and gas phases. R denotes the occurrence of retrograde condensation. In Table II are given the densities and compositions of saturated liquid and of gas for a series of pressures and temperatures. More data are given for the saturated gas because a correspondingly greater number of measurements was made on the dew point than on the saturated liquid boundary. Table III gives critical and cricondentherm (*2*) pressures, temperatures, and densities for a series of compositions.

Table III. Critical and Cricondentherm Data

Composition	Critical			Cricondentherm		
	Temp.	Pressure	Density	Temp.	Pressure	Density
Mole % CH_4	*° C.*	*Atm.*	*Grams /liter*	*° C.*	*Atm.*	*Grams /liter*
10.0	91.0	52.1	232	93.7	48.6	199[a]
20.0	81.2	60.6	232	86.5	53.8	171
30.0	70.9	69.3	232	78.5	58.8	149
40.0	59.3	78.8	231	69.2	63.4	133
50.0	46.3	87.9	231	57.9	67.2	121
60.0	31.1	95.7	229	43.5	70.8	115
70.0	10.4[a]	99.9	225[a]	26.8	73.8	113

[a] Extrapolated.

Discussion of System

In order to aid in visualizing the behavior of the system, a number of typical plots have been drawn from the tabulated data. Figure 2 shows the pressure-temperature relations for three mixtures. The upper part of each curve represents the vapor pressure of a liquid of that composition; the lower part represents the pressure for initial condensation of a gas of that composition. The higher dotted curve is the locus of the critical points, and the lower dotted curve is the locus of the cricondentherms for various compositions. These two curves come together at the critical point of propane, reach a maximum at somewhat lower temperatures than those shown on the plot, and again come together at the critical point of methane. For each composition the point of maxi-

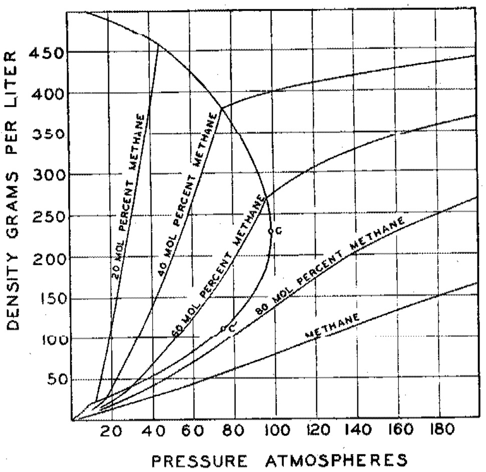

FIGURE 4. CONSTANT COMPOSITION CURVES AT 20° C. ON DENSITY *vs.* PRESSURE DIAGRAM, GIVING BOUNDARY OF TWO-PHASE REGION

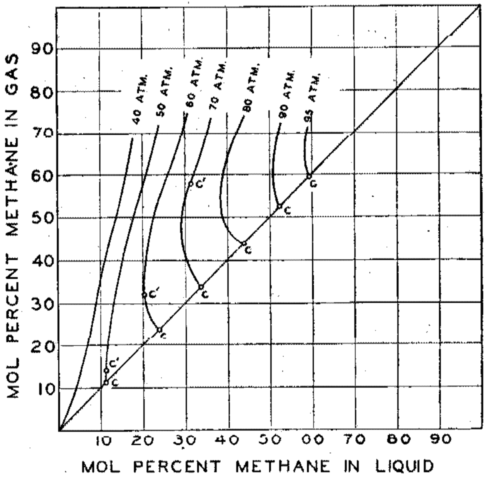

FIGURE 5. CONSTANT PRESSURE CURVES ON GAS COMPOSITION *vs.* LIQUID COMPOSITION DIAGRAM

mum pressure for the existence of two phases occurs at a lower temperature than the critical. This difference in pressure can be seen to increase from zero at the critical point of pure propane to a maximum in the neighborhood of 40 mole per cent methane and again to decrease at higher compositions. From thermodynamic considerations (*4*) this difference would be expected to increase from zero at the critical point of pure propane, pass through a maximum, and again reach zero at the maximum critical pressure of the system. The large region of retrograde condensation of the first kind (normal) between *C* and *C'* is to be expected, owing to the large difference in critical temperatures of the components. The large increase in critical pressure with composition can be attributed to the same reason. Similar phenomena were observed in the case of mixtures of carbon dioxide and hydrogen by Verschaffelt (*7*).

In Figure 3 are shown isothermal plots of the relation of the composition of the saturated gas and liquid to pressure. Again the large region of retrograde condensation is shown, as well as the rapid increase in critical pressure with decreasing temperature. The relative quantity of each phase present for any condition of pressure and total composition can be obtained directly from such plots by consideration of the composition of each phase in relation to the total composition of the system.

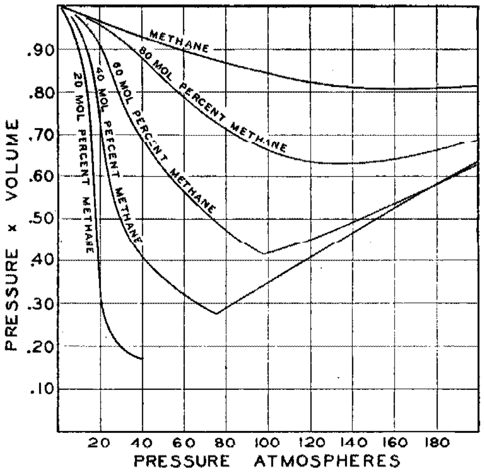

FIGURE 6. CONSTANT COMPOSITION CURVES AT 20° C. ON PERFECT GAS DEVIATION *vs.* PRESSURE DIAGRAM

Figure 4 is a plot at 20° C. of the relations of pressure and density for the entire pressure range studied. The upper part of the boundary curve shows the density-pressure relation for saturated liquid, while the part below *C* shows the same relation for the saturated gas. The total composition lines represent the change in density during the course of an isothermal compression. The curved line connecting the origin with the lower end of the saturated vapor curve represents the density of pure propane in the superheated region. As there were no satisfactory density data for pure propane above 30 atmospheres known to the authors, the lines in the upper part of the liquid region were omitted. The curve for methane was calculated from published compressibility factors (*3*) and agreed closely with that directly determined experimentally. The intersections of the constant-composition lines with the boundary curve give the density and pressure of the saturated liquid and gas of that composition.

In Figure 5 is presented the relation of the composition of liquid and vapor in equilibrium for a series of pressures. The inversion of slope at pressures exceeding 50 atmospheres is due to retrograde condensation. This inversion again disappears as the maximum pressure for the two-phase region is approached. The curves were not continued to higher concentrations of methane since this would necessitate data at temperatures lower than those studied.

From the data in Tables I to III and calculations of the perfect gas densities the compressibilities of given mixtures at various temperatures and pressures can be calculated. The results of such calculations for 20° C. are shown in Figure 6. Again the values for methane were interpolated from published data (*5*) and were plotted for the sake of comparison. The pressure-volume products for each mixture are compared to that of the same mixture at one atmosphere and 20° C. as unity. The breaks in some of the curves are due to the transition from the two-phase liquid-gas region to the one-phase liquid region.

ACKNOWLEDGMENT

The authors express their appreciation to the American Petroleum Institute for financial support furnished for this work.

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RECEIVED August 25, 1933. The data presented in this paper represent work done under Research Project 37 of the American Petroleum Institute.

THE PRESSURE-VOLUME-TEMPERATURE RELATIONS
AND THE
THERMAL PROPERTIES OF PROPANE

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In the study of simple multicomponent systems it is desirable to have the pressure-volume-temperature relations and the thermal properties of each of the components over the pressure and temperature range through which the complex system is studied. Published data on propane one of the important components of industrial hydrocarbon systems is meager, being limited to the properties of the saturated liquid and gas at temperatures below 125°F.(1) and to the measurement of the specific heat at a constant pressure of one atmosphere and temperatures up to the boiling point of water.(4)

Method

In this investigation the specific volume of propane as a function of pressure was measured for a series of systematically varied temperatures. The appearance or the disappearance of a phase was determined by the sharp break in the specific volume-pressure relation at this point. The specific heat at constant pressure as a function of pressure and temperature in the condensed region was measured indirectly by the adiabatic cooling method. A detailed description of the methods and apparatus used in this investigation has been presented by the author in part four of this thesis and will be omitted here.

Material Used

The propane used in this work was obtained from the Philgas Company, Bartlesville, Oklahoma, who submitted a special analysis showing the propane contained no impurities which could be detected by their methods of analysis. The purity of the propane was further tested by isothermal compression and it was found that the dew point and the bubble point were at pressures which differed by less than 0.5 pound per square inch at 100°F. It was also found that the pressure-volume relation at constant temperature yielded very sharp breaks at both the dew and bubble points. From other studies it has been found that small quantities of noncondensible gas markedly obscures the bubble point.

Some of the data obtained is shown in Figure 1.* Most of the points in the superheated region have been omitted due to lack of space on this plot. The points on the isotherms shown were obtained both ascending and descending the pressure scale. On several of these isotherms the points shown were obtained from at least two different samples of propane from the supply mentioned above. In the low temperature region (100°F to 170°F) one sample was used in the superheated region and another in the condensed portion of the isotherm. At higher temperatures a small sample was used up to a pressure of about 250 pounds per square inch, while a larger one was used at higher pressures. Complete isotherms were made at 70°, 100°, 140°, 170°, 200°, 220°F. The higher pressures have been omitted from Figure 1 in order to enlarge the two-phase region on

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* Specific gravity as used in this thesis is defined as the ratio of the weight of a given volume of material to the weight of the same volume of water at its maximum density.

the plot by increasing the scale used. For the determination of the critical constants several short isotherms were made at temperatures above and below the critical temperature covering only the pressure range in the neighborhood of the critical point. The odd temperatures were used here to expedite the attainment of thermal equilibrium. Some of these isotherms are shown on an enlarged scale in Figure 2. The critical constants, which are tabulated in Table 3, were determined from this data. The critical specific gravity* was determined by plotting the average density of the two phases present as a function of temperature, this mean value becomes almost independent of temperature as the critical temperature is approached. A short extrapolation (2°F) to the critical temperature allows accurate determination of the critical density. The slopes of the isotherms above the critical temperature at the critical density were plotted as a function of temperature and the temperature corresponding to zero slope determined. The value thus obtained agreed very well with that obtained by rounding the saturation curves to meet at the critical density. The critical pressure was determined by extrapolating the vapor pressure curve to the critical temperature. The extrapolation was only 0.2°F and as the vapor pressure curve is quite straight in this region the value is believed to be known to at least 1.0 pound per square inch. The vapor pressure of propane as a function of temperature is shown in Figure 3. The data of other observers(1,2,6) has been found to agree fairly well with the reported values.

The laws of ideal solutions appear to apply with reasonable accuracy to equilibrium relations in petroleum mixtures(6,7,8) except for the more volatile component near the critical point for the mixture in question. Other investigators(6,9) have compiled fugacity charts which have been based upon the law of corresponding states for their general application. The fugacity of propane as a function of pressure for a series of temperatures is shown in Figure 4. The fugacity was calculated from the relation(10) $\ln\frac{f_o}{f_1} = \int_0^1 z(d \ln p)$.

The deviation from a perfect gas (z) was plotted against ln p, expressed as PV/RT. Progressive graphical integration of this curve for each temperature yielded the change in fugacity (f_1) as a function of pressure. The fugacity (f_o) was assumed equal to the pressure (p_o) at 1.47 pounds per square inch (0.1 atm). The fugacity of propane thus calculated agrees very well with that computed by other investigators from the law of corresponding states.(7) The fugacity was considered as being of enough importance in equilibrium calculations to warrant tabulation, which has been done for the saturated liquid and gas as well as for the condensed and superheated region, in Tables I and II.

For the calculation of the thermal properties the first derivative of the relation of specific volume to temperature at constant pressure, $(\frac{\partial v}{\partial T})_p$ is important. This relation also affords an excellent check upon the consistency of the data. In Figure 5 is shown the specific volume of superheated propane as a function of temperature at constant pressure. In Figure 6 are shown similar curves on a much enlarged volume scale for the condensed region. The point C on the saturated liquid line being the critical point. In order to obtain the first derivative of these curves they were plotted on as large a scale as consistent with the accuracy of the data and the slopes of the curve measured.

The specific heat of propane was measured indirectly in the condensed region by allowing the liquid to expand adiabatically through a small pressure range and determining the fall in temperature. (see part four of this thesis.) From such measurements and the pressure-volume-temperature data in the condensed region, the specific heat was calculated, using the following relation $\left(\frac{\partial T}{\partial P}\right)_s = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p$. (16) In Figure 7 is shown the specific heat of liquid propane at constant pressure as a function of temperature at a series of pressures. The dotted portions of the curves at the higher temperatures is based upon extrapolated values of $\left(\frac{\partial v}{\partial T}\right)_p$. This extrapolation was necessary because the pressure-volume-temperature data were only determined to 220°F and measurement of slopes at the end of the experimental curves in the critical region is unsatisfactory. The specific heat at the lower temperatures (below 190°F) is believed to be accurate to about 1.5 percent. Each of the points shown is the average of at least six and for the most part ten measurements. The average deviation of the points from the mean value was about 2 percent. The value of the specific heat at the lower temperatures (70°F) is somewhat higher than would have been expected from the extrapolation of the data of other investigators.(1) However, since extrapolation of specific heat under saturation conditions near the critical point of a liquid is somewhat uncertain, the deviation could easily be explained on this basis.

From the data presented, the heat content and the entropy of the saturated liquid and saturated gas, as well as those of the superheated gas and condensed region, can be computed by the method previously described by the author in part 4 of this thesis. These operations have been carefully carried out for propane. The changes in entropy and heat content with temperature were based upon the specific heats at constant pressure reported in this thesis. The results of these calculations for the saturated liquid and gas are presented in Table II, along with the specific volume and the ratio of the fugacity to pressure which is the same for both the saturated liquid and gas. Similar data for the condensed and the superheated regions are reported in Table IV. In the condensed region both the entropy and the heat content were carried at least one place farther than warranted by the specific heat measurements. This was done to allow the more accurate evaluation of the isothermal changes in these properties which are known much more precisely than the change with temperature. The changes in heat content and entropy at low pressure (25 pounds per square inch) agrees well with those calculated from specific heat measurements made by other investigators(4) at atmospheric pressure. Both the entropy and heat content of the saturated liquid were set equal to zero at 60°F. In Figure 8 is shown the deviation of the tabulated heat content of the saturated liquid and gas from that of other investigators.(1) The deviation was based upon placing the heat content of the saturated liquid at 60°F of both sets of data equal. The lower values reported by the Linde Laboratory are due to their lower values of extrapolated specific heat. The much larger deviation of the heat content of the saturated gas is due to the divergence of the latent heats of vaporization which are shown in Figure 9. The values of the Linde Laboratory were directly measured and indicate a somewhat higher value for the latent heat than was obtained by application of the Clapeyron equation to the reported data. Since the data of the Linde

Laboratory was extrapolated some distance in order to obtain their reported values at the upper end of their temperature range (125°F) the agreement is considered satisfactory.

Many ways of presenting graphically the thermal properties and the pressure-volume-temperature relations are available. When both the condensed and superheated regions are included, however, the temperature-entropy plane affords several advantages. This plane was chosen for this presentation and the other three important variables, pressure, volume and heat content, were included as lines on this plane. A small reproduction of this chart is shown in Figure 10, having been drawn to such a scale that the accuracy of plotting was equal to that of the tabulated data in all but the condensed region; a full-size contact print of this chart has been included in an envelope at the end of this thesis.

Conclusions

The work reported in this thesis has indicated that:

(1) The apparatus used in this work, described elsewhere by the author, is well suited to the measurement of the pressure-volume-temperature and thermal properties of a pure hydrocarbon in the critical region.

(2) The determination of the critical pressure and temperature without a knowledge of the critical density is open to question.

(3) The law of corresponding states appears to apply to the thermal properties of propane almost as well as to the measured physical properties.

(4) The indirect measurement of the specific heat at constant pressure, by adiabatic expansion in the condensed region, yields satisfactory results at temperatures close to the critical and at pressures as low as twice the critical value.

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TABLE I.

Physical and Thermal Properties of Propane

Superheated Gas and Condensed Liquid Regions

p = pressure in lbs. per sq.in. absolute
v = specific volume in cu.ft. per lb.
f = fugacity in lbs. per sq.in.
h = heat content in Btu per lb.
s = entropy in Btu per lb. per ° Fahrenheit Absolute

p	70°F				100°F				130°F				160°F				190°F				220°F				p
	v	f/p	h	s	v	f/p	h	s	v	f/p	h	s	v	f/p	h	s	v	f/p	h	s	v	f/p	h	s	p
25	4.997	0.9731	161.7	0.3715	5.307	0.9761	174.4	0.3948	5.610	0.9800	187.3	0.4171	5.913	0.9826	200.4	0.4402	6.224	0.9859	214.3	0.4607	6.531	0.9884	228.4	0.4813	25
50	2.417	.9435	160.5	.3388	2.578	.9516	173.2	.3624	2.740	.9579	186.1	.3849	2.899	.9639	199.3	.4070	3.056	.9703	213.2	.4280	3.217	.9761	227.4	.4488	50
75	1.552	.9149	158.2	.3175	1.664	.9274	171.4	.3414	1.731	.9364	184.4	.3652	1.894	.9449	197.8	.3875	2.002	.9533	211.9	.4086	2.107	.9620	226.1	.4293	75
100	1.113	.8855	154.9	.3001	1.208	.9011	169.2	.3254	1.298	.9158	182.8	.3505	1.386	.9266	196.3	.3732	1.471	.9372	210.4	.3945	1.556	.9473	224.6	.4148	100
125	0.841	.8559	148.4	.2809	0.9332	.8743	166.3	.3118	1.014	.8933	180.6	.3381	1.085	.9081	194.8	.3614	1.155	.9212	208.8	.3825	1.222	.9332	223.2	.4031	125
150					0.7494	.8491	162.8	.2986	0.8094	.8728	178.4	.3271	0.8830	.8897	193.0	.3507	0.9424	.9036	207.1	.3724	1.000	.9174	221.6	.3932	150
175					0.6118	.8247	158.7	.2871	0.6826	.8519	176.1	.3175	.7366	.8708	191.2	.3426	.7895	.8884	205.4	.3636	0.8422	.9055	220.1	.3844	175
200	0.03174	.5509			0.03368	.7386	27.15	.05041	0.5744	.8333	174.0	.3084	.6253	.8535	189.3	.3344	.6734	.8722	203.9	.3558	.7215	.8904	218.6	.3767	200
225									0.4905	.8129	171.4	.2999	.5408	.8351	187.4	.3269	.5803	.8567	202.3	.3490	.6309	.8769	217.0	.3697	225
250		.4518				.6315			0.4200	.7904	167.5	.2908	.4707	.8160	185.4	.3198	.5145	.8400	200.5	.3427	.5556	.8632	215.5	.3632	250
275													.4154	.7992	183.0	.3129	.4559	.8244	198.9	.3362	.4931	.8482	214.0	.3572	275
300	0.03159	.3741	6.65	.0109	0.03347	.5209	26.99	.04903	0.03534	.7048	48.34	.08596	.3657	.7616	180.7	.3058	.4051	.8091	197.2	.3303	.4420	.8363	212.3	.3517	300
350													.2856	.7461	172.9	.2893	.3395	.7759	193.3	.3190	.3641	.8089	209.4	.3471	350
400	0.03147	.2879	6.66	.0100	0.03329	.4060	26.91	.04775	0.03554	.5420	47.98	.08424	.03919	.6907	71.27	.12292	.2729	.7457	188.5	.3075	.3174	.7801	206.4	.3335	400
450																	.2215	.7144	182.2	.2951	.2528	.7575	203.7	.3257	450
500	0.03134	.2349			0.03311	.3308			0.03523	.4457			.03852	.5072			.1701	.6931	172.1	.2770	.2150	.7212	199.8	.3176	500
550																			101.3		.1807		195.7	.3036	550
600	0.03123	.2017	6.68	.0081	0.03294	.2822	26.80	.04538	0.03498	.3799	47.45	.08115	.03795	.4353	69.49	.11764	.04354	.5801	99.40	.15441	.1447		190.6	.2980	600
700	0.03112	.1771			0.03277	.2441			0.03474	.3345			.03746	.4073			.04241	.5177							700
800	0.03102	.1589			0.03262	.2222	26.78	.04313	0.03452	.3002	47.10	.07839	.03705	.3721	68.33	.11348	.04109	.4696	95.51	.15694					800
900	0.03092	.1445			0.03241	.2032			0.03430	.2713			.03665	.3454			.04056	.4253							900
1000	0.03083	.1331	7.10	.0045	0.03233	.1862	26.84	.04113	0.03410	.2504	46.90	.07588	.03629	.3217	67.56	.11006	.03945	.3719	93.35	.15003			134.23	.2115	1000
1250	0.03062	.1129			0.03202	.1578	27.00	.03874	0.03363	.2131	46.81	.07306	.03554	.2731	66.97	.10645	.03819	.3331	91.59	.14513	.0423	.408			1250
1500	0.03043	.0998	7.60	.0003	0.03175	.1398	27.22	.03650	0.03325	.1866	46.87	.07051	.03495	.2406	66.66	.10331	.03724	.2961	90.40	.14060	.0406	.362	124.45	.1922	1500
1750	0.03026	.0908			0.03151	.1272	27.08	.03439	0.03291	.1699	47.03	.06816	.03447	.2188	66.53	.10049	.03652	.2708	89.57	.13668	.0395	.328			1750
2000	0.03010	.0864	8.30	-.0033	0.03129	.1177	28.02	.03241	0.03261	.1580	47.26	.06595	.03407	.2029	66.53	.09791	.03513	.2513	88.99	.13318	.0386	.305	120.18	.1807	2000
2250	0.02996	.0791			0.03109	.1107			0.03232	.1488			.03607	.1903			.03540	.2357			.0377	.288			2250
2500	0.02983	.0756	9.58	-.0066	0.03093	.1053	28.54	.02870	0.03207	.1413	47.57	.06187	.03334	.1812	66.83	.09335	.03491	.2243	88.29	.12703	.0370	.275	117.70	.1713	2500
2750	0.02971	.0723			0.0376	.1014			0.03134	.1363			.03303	.1742			.03448	.2157			.0364	.265			2750
3000	0.02960	.0704	10.25	-.0094	0.03004	.0983	29.30	.02528	0.03164	.1317	48.24	.05821	.03275	.1677	67.39	.08935	.03412	.2078	88.10	.12163	.0358	.255	116.50	.1644	3000

TABLE II

Physical and Thermal Properties of Propane

Saturated Liquid and Saturated Gas

t = temperature in °F; other units as in Table I

p	t	Saturated gas			Saturated liquid			f/p
		v	h	s	v	h	s	
125	69.4	0.8388	147.7	0.2799	0.03185	6.2	0.0123	0.8555
150	82.3	.6936	151.2	.2800	.03260	14.8	.0287	.8357
175	93.8	.5922	154.2	.2801	.03333	22.7	.0428	.8182
200	104.3	.5152	156.8	.2802	.03403	30.2	.0556	.8039
225	113.8	.4535	158.9	.2803	.03471	36.9	.0671	.7913
250	122.4	.4050	160.8	.2801	.03535	42.9	.0776	.7803
275	130.6	.3648	162.3	.2796	.03601	48.9	.0871	.7698
300	138.1	.3278	163.6	.2789	.03668	54.3	.0960	.7590
325	145.3	.2973	164.4	..2779	.03743	59.7	.1048	.7483
350	152.1	.2704	165.0	.2768	.03822	65.1	.1131	.7379
375	158.6	.2460	165.3	.2752	.03907	70.3	.1216	.7263
400	164.8	.2242	165.5	.2739	.03997	75.5	.1300	.7160
425	170.5	.2039	165.5	.2724	.04089	80.7	.1380	.7057
450	175.9	.1856	165.3	.2707	.04191	86.0	.1461	.6962
475	180.9	.1692	165.0	.2690	.04296	91.2	.1542	.6857
500	185.8	.1545	164.5	.2672	.04415	97.1	.1624	.6793
525	190.6	.1402	163.9	.2652	.04556	103.1	.1714	.6708
550	195.1	.1281	163.2	.2631	.04713	109.2	.1800	.6635
575	199.6	.1176	162.5	.2609	.04905	116.2	.1873	.6555
600	204.1	.1041	161	.258	.05163	123.6	.201	.6471
625	208.5	.0896	158	.253	.05577	133	.214	.639

TABLE III

Critical Constants of Propane

Pressure, 643.3 lbs. per sq.in. absolute

Temperature, 212.2°F

Specific Volume, 0.06896 cu.ft. per lb.

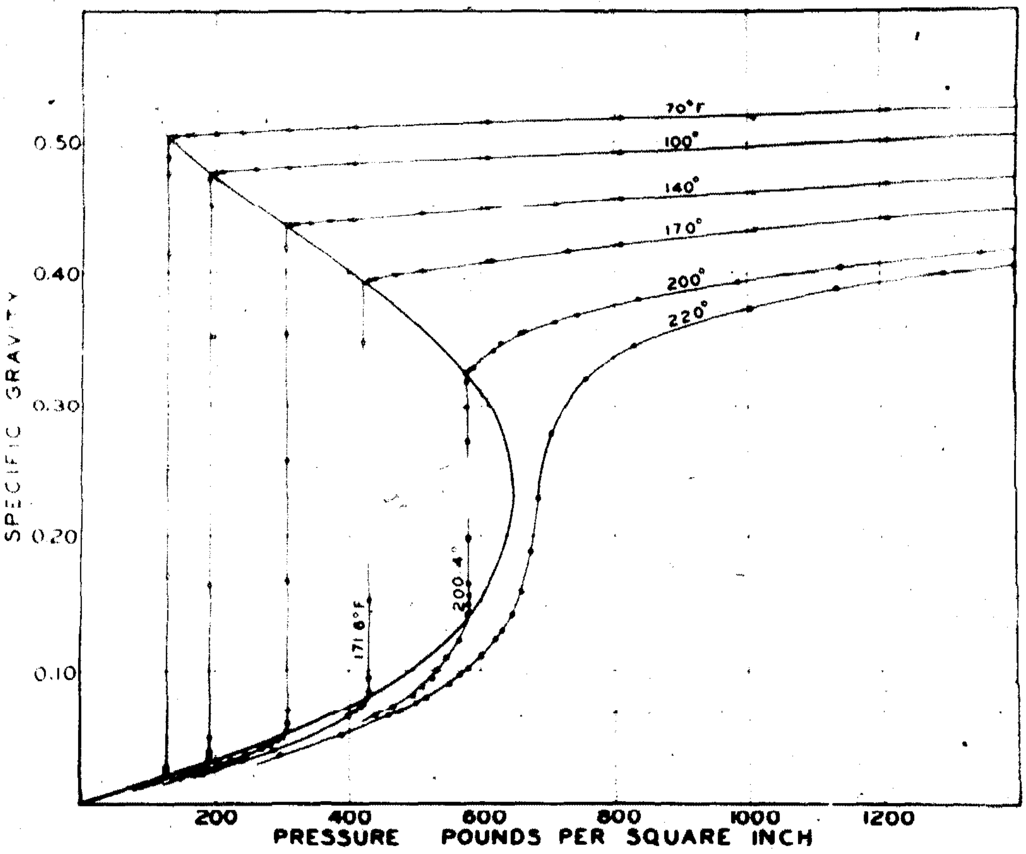


Fig. 1

Propane Isotherm

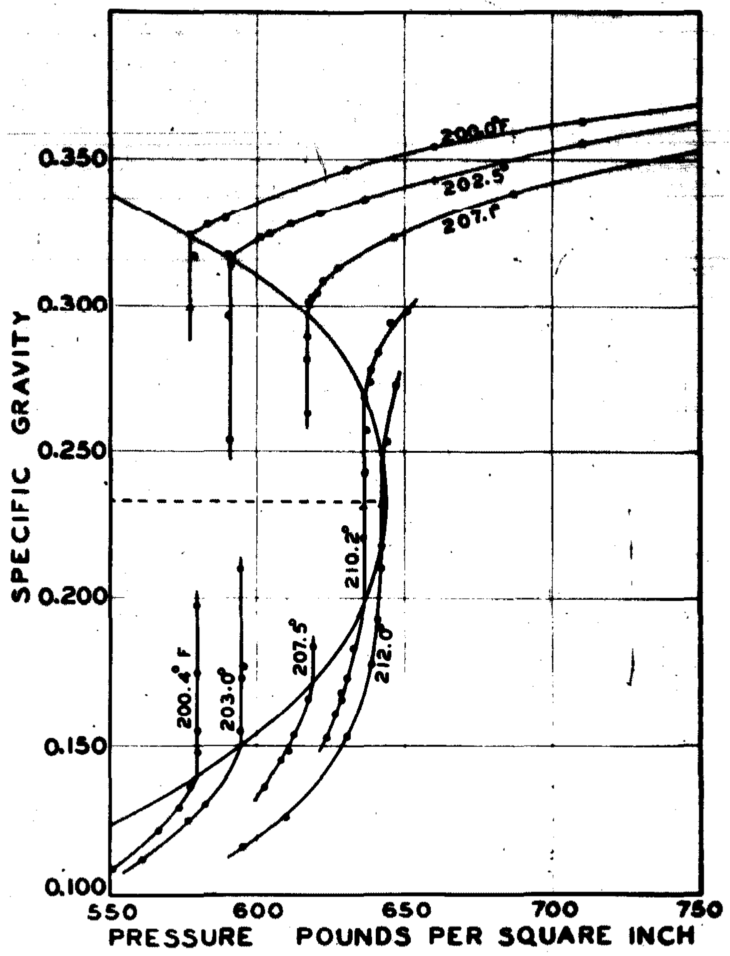


Fig. 2

Isotherms in Critical Region

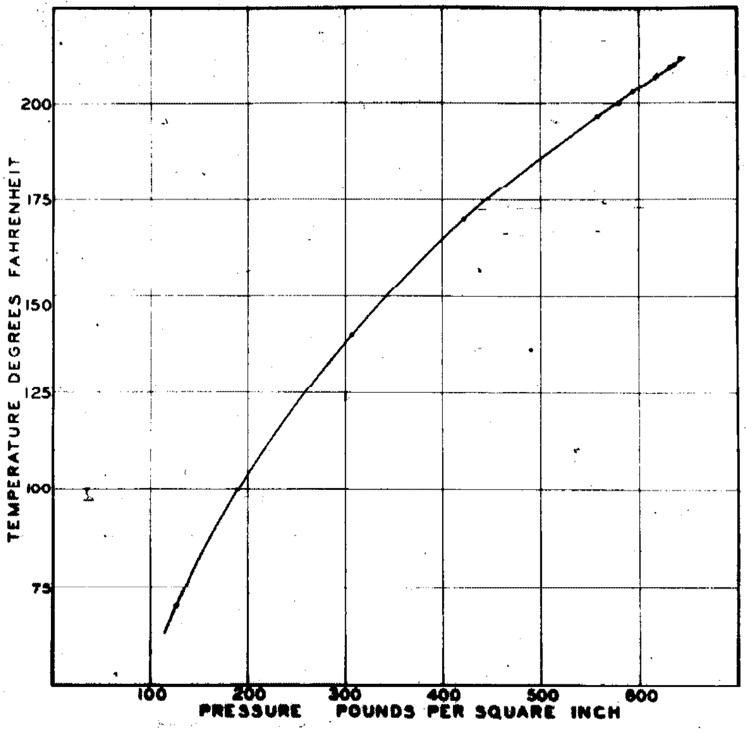


Fig. 3

Vapor Pressure of Propane

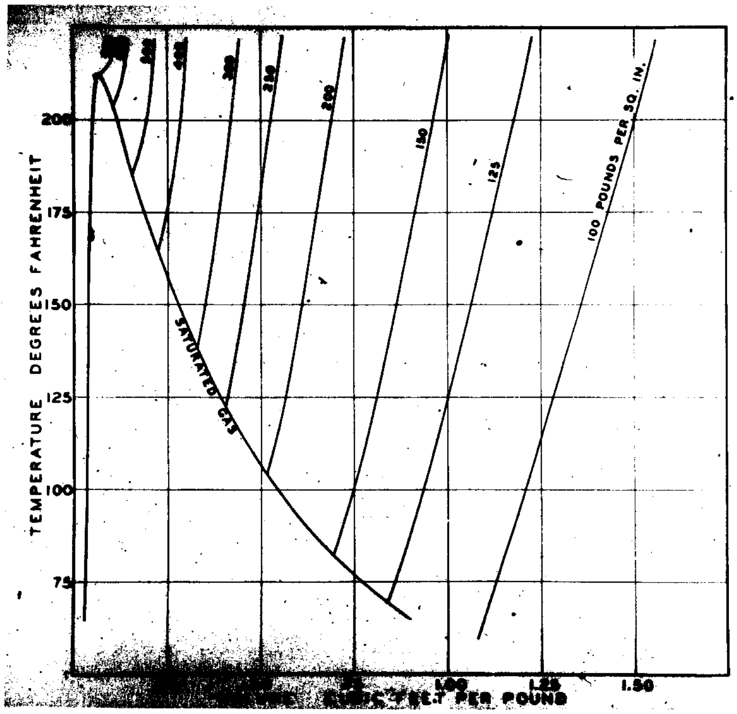


Fig. 5

Specific Volume of Propane

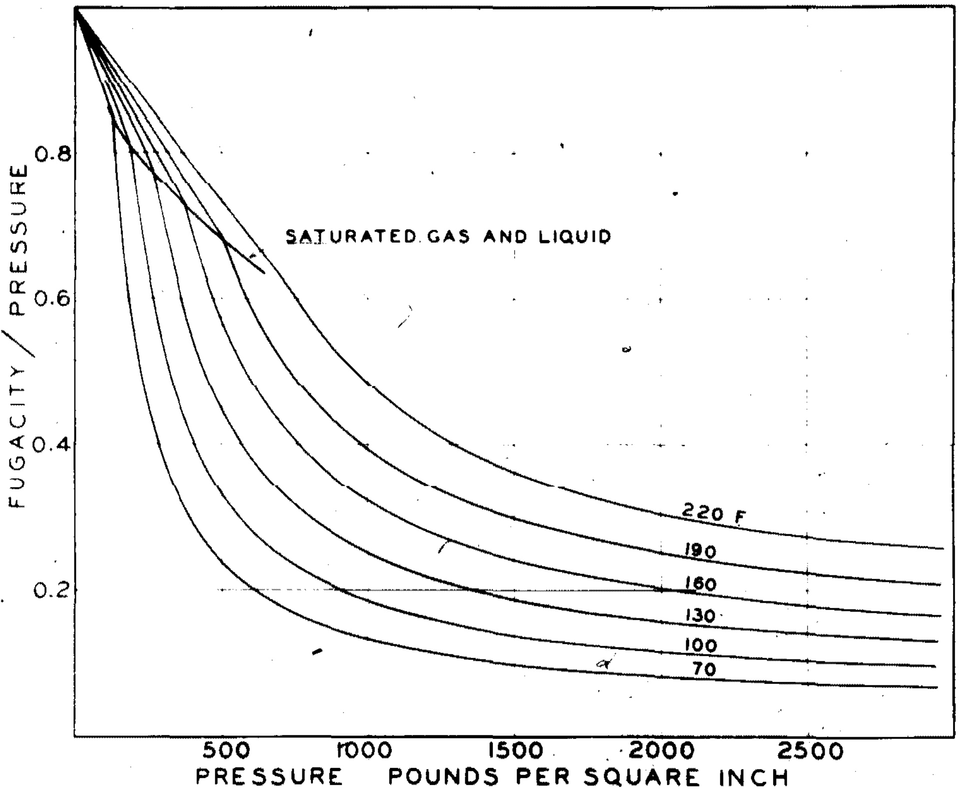


Fig. 4

Fugacity of Propane

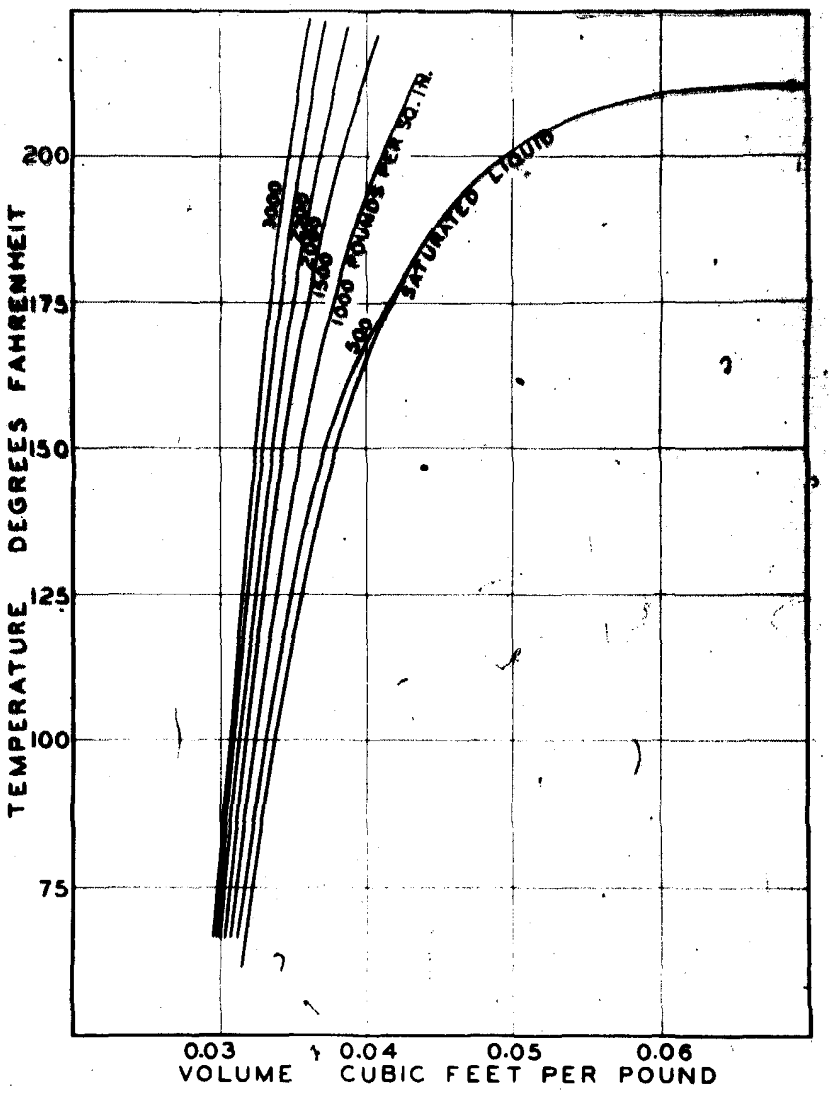


Fig. 6

Specific Volume of Liquid Propane

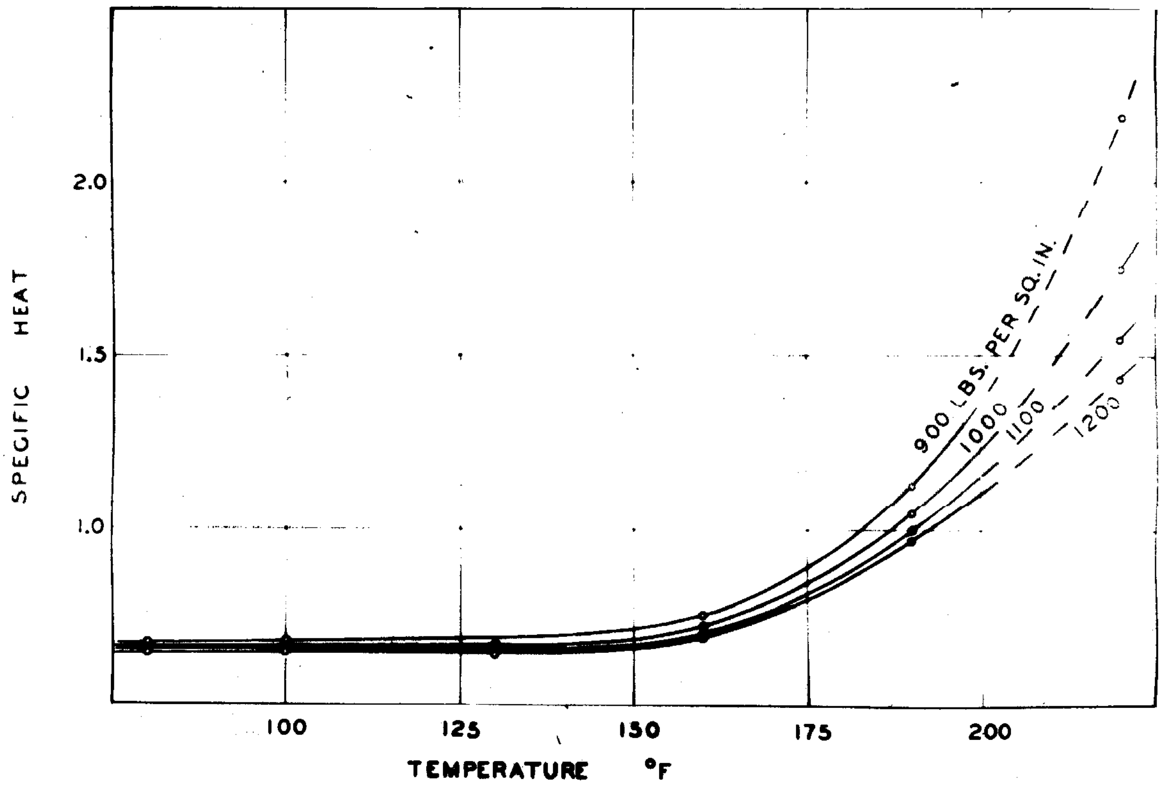


Fig. 7

Specific Heat at Constant Pressure
of Liquid Propane

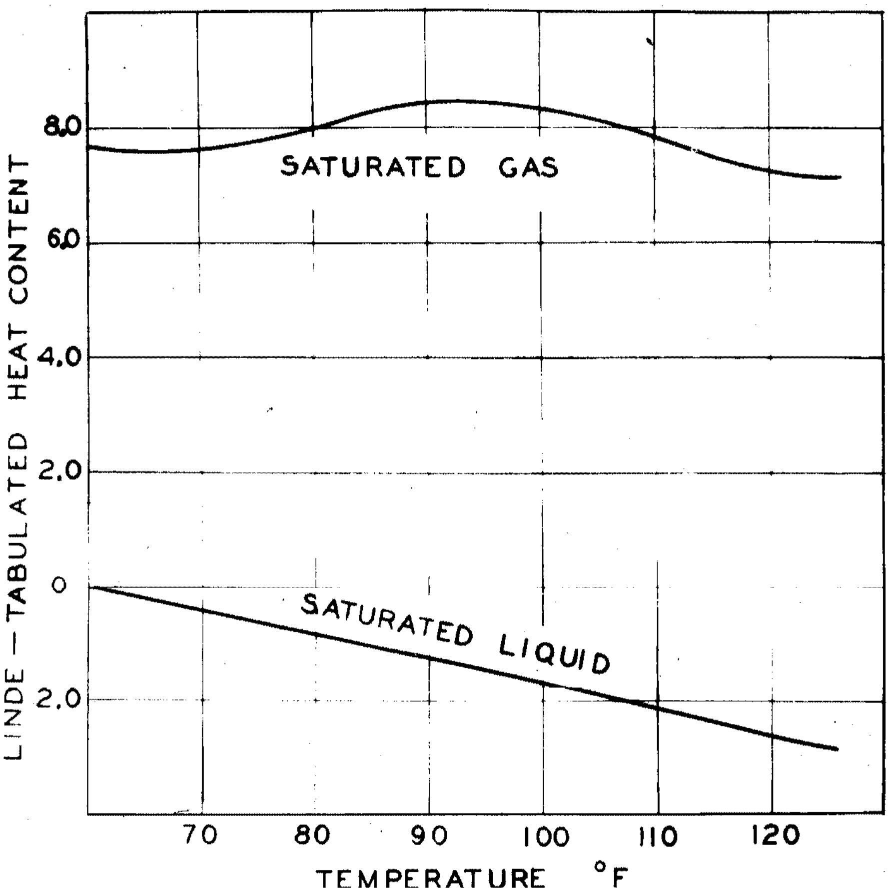


Fig. 8

Deviation of Tabulated Heat Content from that of Other Investigators

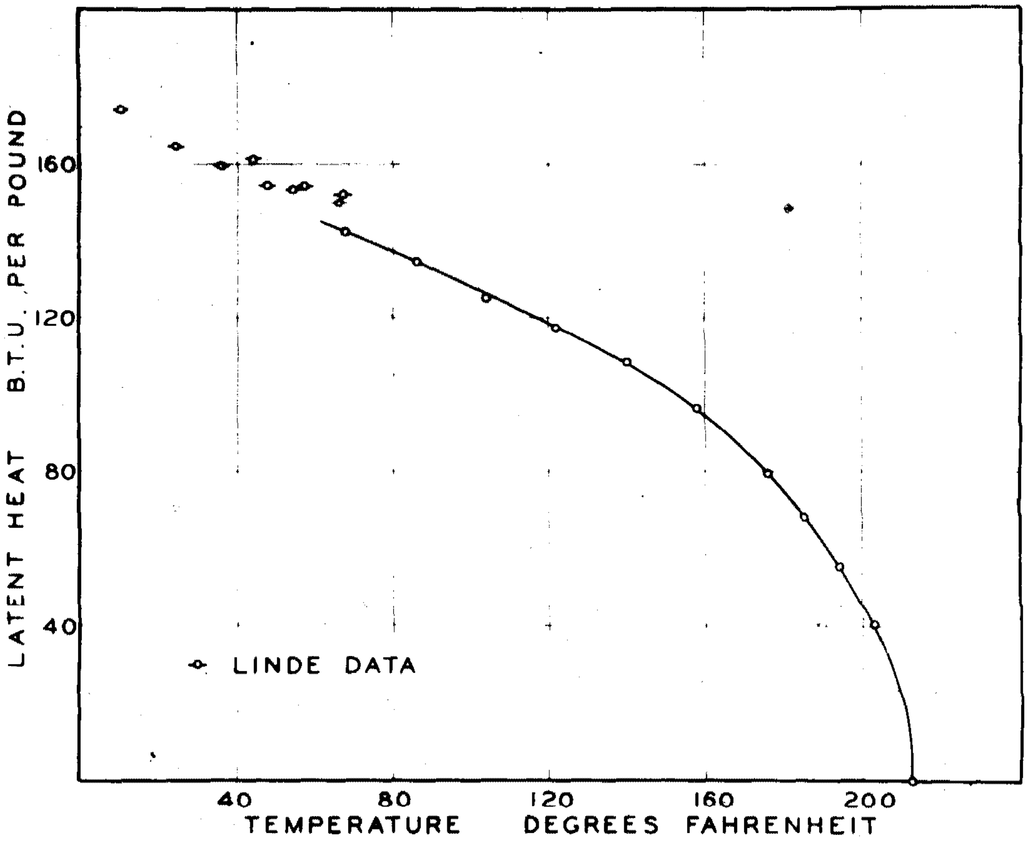


Fig. 9

Heat of Vaporization of Propane

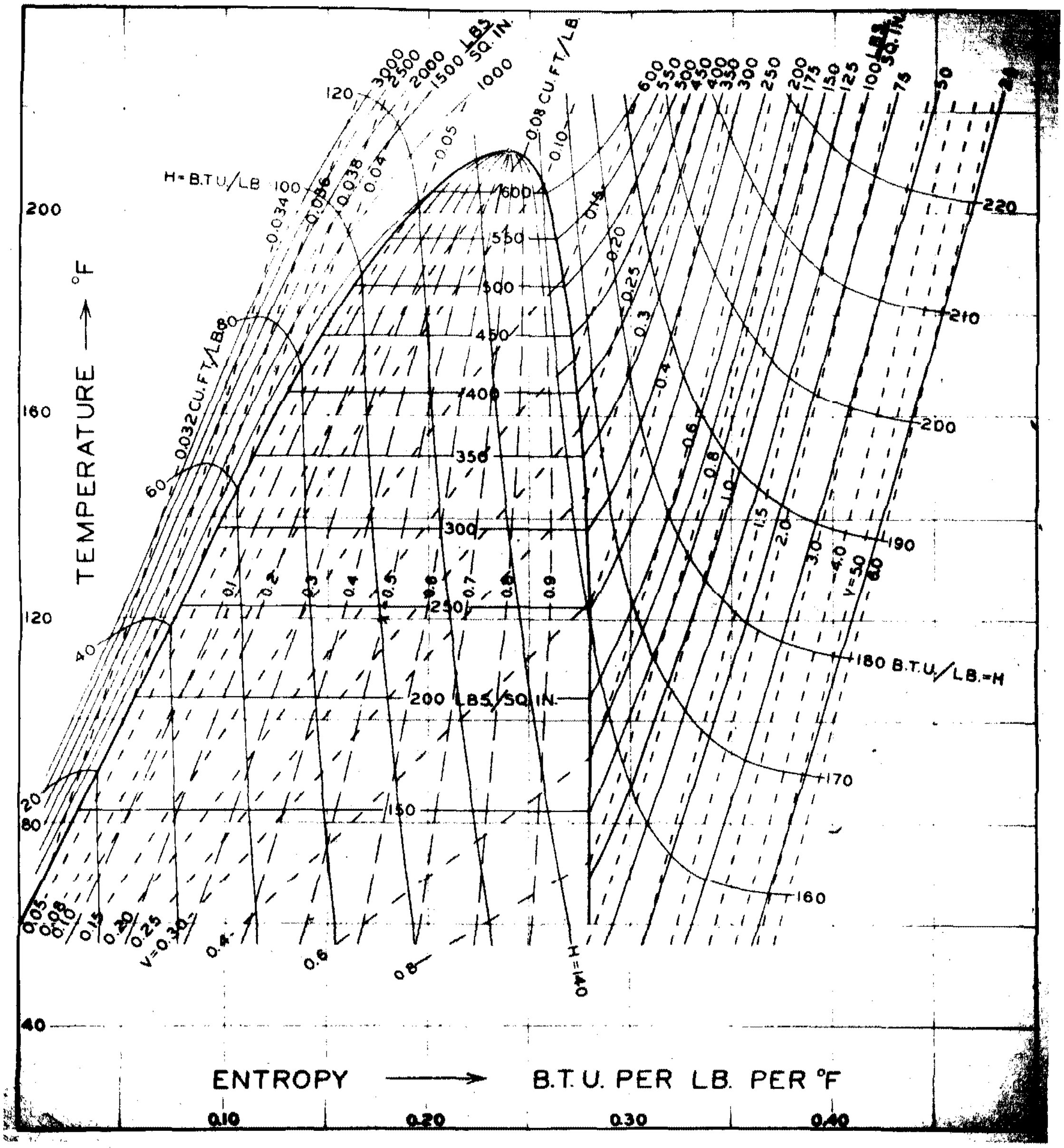


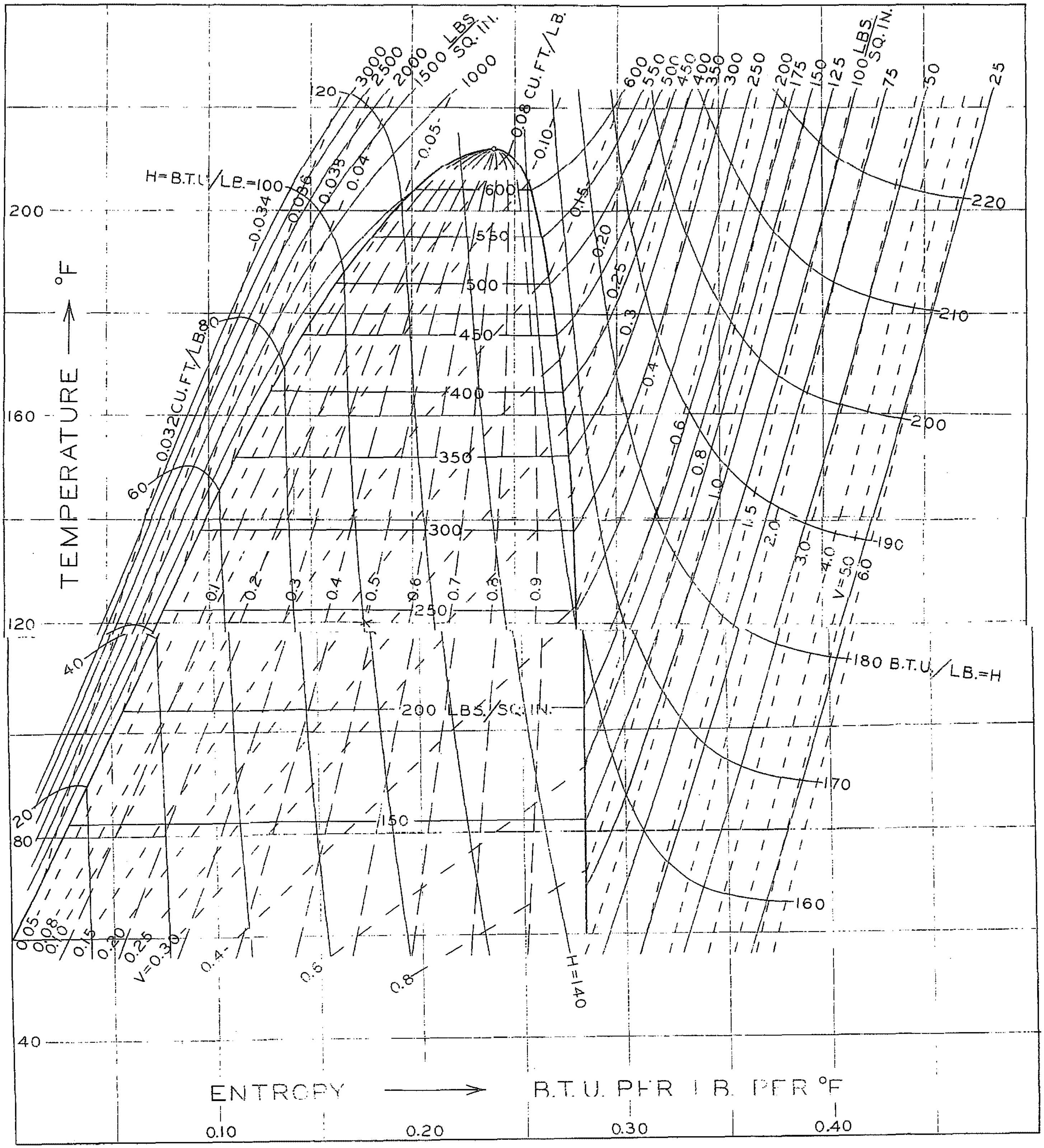
Fig. 10

Temperature Entropy Diagram for Propane

Pg. 61 is missing.

Acknowledgements

The experimental work reported in this thesis was carried out under Research Project Number 37 of the American Petroleum Institute, to whom the author wishes to express his thanks for financial support of the work. To Dr. W.N.Lacey credit is due for his assistance and advice in carrying out the measurements reported in this thesis. Thanks are due to Mr. J.G.Schaafsma for aid in both the experimental work and in the preparation of the charts and tables here presented.



PROPERTIES OF PROPANE