

Values along the abscissa of Figures 3 and 4 may be used as multiplying correction factors to be applied to factor C obtained from Figure 1, according to the type of service, such as gas absorbers, fractionating section of oil strippers, petroleum columns, and gasoline stabilizers as indicated on the figures. These values should be considered as tentative but represent the best available data for the maximum mass vapor velocity consistent with good operation of columns of adequate mechanical design. Special conditions or products demand individual consideration of the permissible entrainment on the basis of the factors discussed above.

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RECEIVED July 17, 1933. This article is a combination of papers presented, respectively, before a joint meeting of the Chicago Section and the Petroleum Division of the American Chemical Society, Chicago, Ill., January 22, 1932, and before the Petroleum Group at the Sectional Meeting of the Society, St. Louis, Mo., May 5, 1932.

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.

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

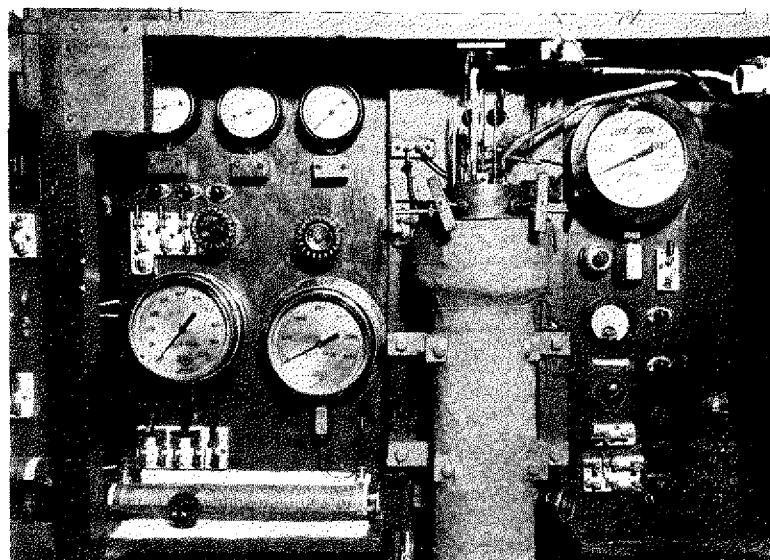


FIGURE 1. COMPRESSOR AND CONTROL PANEL

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 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.

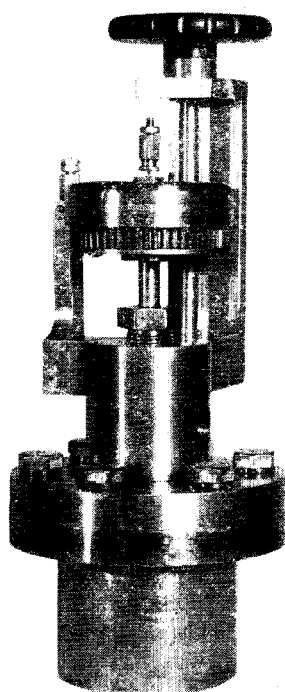


FIGURE 2. EQUILIBRIUM CELL

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

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

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

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.

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-

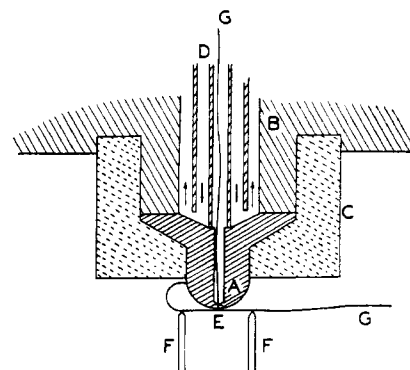


FIGURE 3. DEW POINT APPARATUS

controlled to the temperature at which measurements were being made.

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,

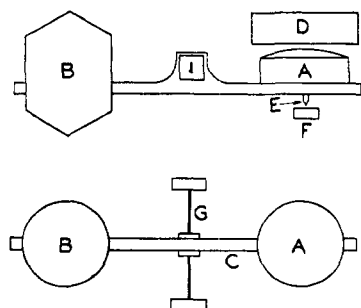


FIGURE 4. ELEVATION AND PLAN OF GAS DENSITY BALANCE

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

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.

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.

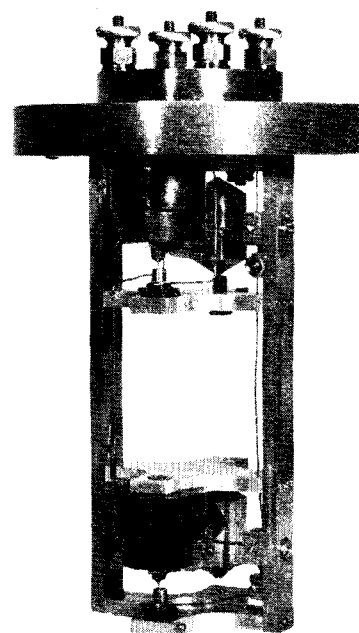


FIGURE 5. DENSITY BALANCE ASSEMBLY

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

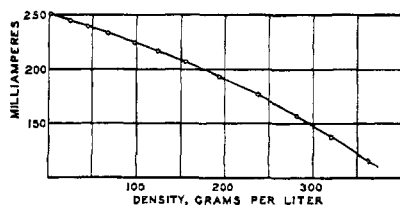


FIGURE 6. DENSITY BALANCE CALIBRATION CURVE

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.

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.

RESEARCH FOR PROGRESS. In the annual report to his board of trustees, Doctor John C. Merriam, president of the Carnegie Institution of Washington, says, in part:

"In the history of this country, the place of research among factors touching needs of advancing civilization is illustrated by its relation to the broader features of our economic experience. Abundant development of natural resources has produced great wealth and the advantages which flow from it. The period of harvesting these materials has been followed by one of extraordi-

nary mechanical and industrial growth. At the present moment the natural resources are well known and adjusted to future use. Further advance depends largely upon research, inventive genius, and human organization. New ideas ranging from those arising out of physics, chemistry, and biology on into laws of history, problems of economics, social values, governmental principles, and the more fundamental understanding of human behavior have come to take primary place in classification of our needs."