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THE ANALYTICAL DISTILLATION OF PETROLEUM AND ITS PRODUCTS

BY

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CONTENTS.

Methods for determining physical properties of distillation fractions—Con.

Specific-gravity determination—Continued.

TABLES.

ILLUSTRATIONS.

THE ANALYTICAL DISTILLATION OF PETROLEUM AND ITS PRODUCTS.

By E. W. Dean, H. H. Hill, N. A. C. Smith, and W. A. Jacobs.

INTRODUCTION.

Fractional distillation is the most important process in the commercial refining of petroleum. The same procedure, conducted on a small scale, is the basis of a number of analytical methods of wide application in the petroleum laboratory. The Bureau of Mines has studied apparatus and procedure for the distillation analysis of petroleum, and this report is presented as a record of developments up to the present time. The work is incomplete, but the extensive information that has been obtained to date is made available as a guide in handling laboratory distillation problems.

The analytical distillation of petroleum is commonly made to determine range of boiling points or to separate the oil into fractions for detailed examination, or both. When only one of these two ends is sought the procedure involved is notably simpler than when, as is more common, information is required regarding both boiling range and properties of fractions. Moreover the degree of minuteness of measurement and the accuracy of the data required from analytical distillations differ considerably. Often the simplest sort of comparative figures are satisfactory; other tests require complicated and highly tedious procedure. No one distillation method is universally applicable, and it is impossible for any one group of investigators to foresee all the different kinds of requirements that may occur in the industry.

DISTILLATION OF CRUDE PETROLEUM.

The Bureau of Mines has already issued several publications on analytical distillation. The method first recommended[1] was developed in connection with a study of California crude petroleum, but

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[1] Allen, I. C., and Jacobs, W. A., Physical and chemical properties of the petroleums of the San Joaquin Valley, Calif., with a chapter on analyses of natural gas from the southern California oil fields, by G. A. Burrell: Bull. 19, Bureau of Mines, 1911, 60 pp., 2 pls., 10 figs. Allen, I. C., Jacobs, W. A., Crossfield, A. S., and Matthews, R. R., Physical and chemical properties of the petroleums of California: Tech. Paper 74, Bureau of Mines, 1914, 38 pp., 1 fig.

was later discarded as further study[2] showed that refinable crudes required apparatus including some sort of a fractionating column or "still head." The type of still head that seemed most desirable was a variety of the familiar "Hempel column." The same procedure has been somewhat modified after several years of use in the laboratories of the bureau is now recommended, but the changes involve details of operation rather than general principles.

DISTILLATION OF REFINED PRODUCTS.

The bureau has recommended a distillation method for testing gasoline and certain other refined products. The requirements of this particular type of analysis, namely, a convenient and moderately accurate basis of comparison, are notably different from those of the analysis of crude petroleum. The modified A. S. T. M. method recommended by the bureau[3] and adopted by various organizations and laboratories, provides a simple means of comparing the range of boiling points of different samples. It is not designed to separate fractions for detailed examination, and although used for this purpose at times is not as satisfactory as other methods. It is used and recommended by the bureau for the testing of a variety of refined products including gasoline, naphtha, and kerosene, for which the temperature to be measured does not exceed about 320° C. (608° F.). It could also be used for other products to measure distillation range up to some mark not in excess of 320° C., above which cracking is likely to occur.

The present report describes the apparatus and methods used by the bureau for the routine distillation analysis of crude oil and lubricating oil and describes also apparatus developed for certain types of research. Some of the methods for studying the fractions separated are described, also for dehydrating emulsified oils, which is often a necessary preliminary to analytical distillation.

ROUTINE DISTILLATION OF CRUDE PETROLEUM AT ATMOSPHERIC PRESSURE.

APPARATUS.

ELECTRIC HEATERS.

Electric heaters are used for practically all petroleum distillations made by the Bureau of Mines. The type of heater now in use is described in detail.

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[2] Rittman, W. F., and Dean, E. W., The analytical distillation of petroleum: Bull. 125, Bureau of Mines, 1916, 79 pp., 1 pl., 16 figs.; The analytical distillation of petroleum: Jour. Ind. and Eng. Chem., vol. 7, pp. 185–195, 754–760.

[3] Dean, E. W., Motor gasoline; properties, laboratory methods of testing, and practical specifications: Tech. Paper 166, Bureau of Mines, 1917, 27 pp.; Motor gasoline; properties, laboratory methods of testing, and practical specifications: Tech. Paper 214, Bureau of Mines, 1919, 33 pp., 2 figs.

Figure 1 shows construction details of the heating element.

A flanged, hemispherical, hollow wooden form is made with the same outside diameter as the bulb of the distillation flask. Starting at the center of the outer hemispherical surface a spiral of about 4½ turns is marked off. Small holes are drilled through the mold at points about an inch apart along this spiral line. The mold is coated with shellac and is generally smeared with petrolatum or heavy lubricating oil as an additional protection.

A suitable length of resistance wire is wound in a helix on a mandrel approximately one-eighth inch in diameter. The authors tried several grades of resistance wire, all of which gave good service. The type generally used is an alloy composed of 80 per cent nickel and 20 per cent chromium, with a resistance of 620 ohms a circular mil foot. Several other nickel-chromium alloys covered by the Marsh patents have been used, also two alloys that are not covered by these patents.

The patented nickel-chromium alloys are undoubtedly preferable but heaters made with the cheaper wires have successfully passed service tests. In types of heaters for routine distillation of crude petroleum and lubricating oil the resistance element does not work at an excessively high temperature. The unpatented wire may prove satisfactory for some of the types of heaters described for other purposes, but it has not been tested under such conditions by the authors.

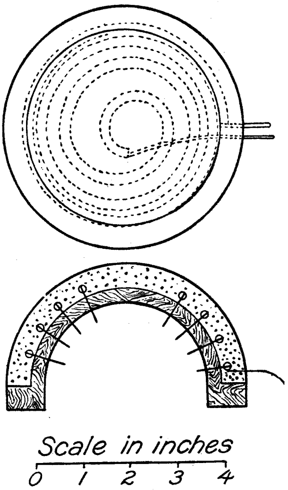

FIGURE 1.—Plan and section of the heating element of electric heater showing wooden mold, helix of resistance wire held by brads, and alundum cement.

Table 1 gives the trade names, the manufacturers, and the resistance for several grades of wire suitable for electric distillation heaters.

TABLE 1.—*Resistance wire for electric heaters.*

GROUP 1: NICKEL-CHROMIUM ALLOYS, COVERED BY THE MARSH PATENTS.

Name of wire.	Manufacturer.	Resistance, ohms per circular mil foot at 75° F.
Nichrome	The Driver-Harris Co., Harrison, N. J	660
Nichrome II	do	660–680
Kromore	do	580–610
Calido	The Electrical Alloys Co., Morristown, N. J	620
Rayo	do	575
Chromel C	The Hoskins Manufacturing Co., Detroit Mich	650
Chromel B	do	535
Chromel A	do	620

GROUP 2: ALLOYS OF MODERATELY HIGH RESISTANCE AND MELTING POINT, NOT RESTRICTED BY THE MARSH PATENTS.

No. 193 alloy	The Driver-Harris Co., Harrison, N. J	525
Comet	The Electrical Alloys Co., Morristown, N. J	525

The price of the wire made by each company increases down the list; thus Kromore is more expensive than Nichrome. The prices listed for the several companies for a given grade of wire are approximately the same.

Private laboratories frequently have difficulty in purchasing resistance wire covered by the Marsh patents. Arrangements for obtaining wire to be used in experimental work can often be made by filing a proper application with the Hoskins Manufacturing Co., Detroit, Mich.

The properties of suitable resistance elements and the sizes and lengths of the wire comprising them are shown in Table 2.

TABLE 2.—*Construction details and properties of resistance elements.*

	Voltage of current.	B. and S. gage of wire.	Feet of wire to be used.	Resistance in ohms (approximate).	Amperes carried.	Watts.
Alloys in Group 1	110	18	45	18	6.1	670
Do	220	22	70	70	3.1	680
Alloys in Group 2	110	19	45	18	6.1	670
Do	220	23	70	72	3.1	670

The helix is stretched to a length equal to that of the spiral laid off on the mold, about 40 inches. It is then placed on the mold and held in place by points of brads that have been pushed from the inside through the holes drilled along the spiral line. The ends of the helix are held firmly by wrapping the wire several times around larger brads that project about $\frac{1}{2}$ an inch. The other brads should not project farther than the diameter of the helix.

A very thick paste of alundum cement and water is prepared and the mold and helix is covered with this. The paste should be worked in well between the turns of the helix and the total thickness of the layer should be about five-eighths of an inch. The cement is allowed to dry at room temperature for from 1 to 3 days, when the mass becomes firm enough to permit handling although still decidedly fragile. The brads are carefully withdrawn from the inside and the heating element, wooden mold and all, is placed for a few minutes in an oven heated to a temperature of about 100° C. (212° F.), to contract the wooden mold enough to permit its removal. The interior of the alundum mass is then made smooth with a thin paste of the cement, after which the heating element is placed in the oven again and allowed to dry for several hours at a temperature of 100 to 150° C. (212 to 302° F.). Finally, it is fired for about 30 minutes in a muffle furnace at a temperature of 700 to 900° C. (1292 to 1652° F.), or, if no satisfactory furnace is available, it may be brought cautiously to red heat by connecting it with a properly regulated electrical current. After this final heating it is hard and as durable as ordinary stoneware.

Several types of supporting cases for electric heaters have been tried by the bureau and a form that seemed very satisfactory is shown in figure 2. The case is of brass or any other suitable metal, is shaped like the frustrum of a cone, and has a gasket-like top of hard asbestos or "transite" board.

A special kieselguhr composition,[4] generally sold in the form of bricks, has proved to be a good insulator. These bricks can be shaped roughly to the desired forms and the interstices filled with brick dust. Shredded asbestos, plain kieselguhr, or magnesia can, if desired, be used instead of the special composition bricks.

The method of assembling the heater is indicated in figure 2. The heating element is attached to the cover by a strap of sheet metal held in place by small "stove bolts." The transite cover is attached to the metal case by stove bolts.

The heaters are generally used in series with regulating rheostats capable of reducing the effective wattage to about one-fourth to one-third the full load maximum. For 110-volt current a rheostat of 15 to 20 ohms and six amperes has proved satisfactory; for 220-volt current 70 ohms and three amperes are needed. Satisfactory rheostats are readily obtainable from chemical supply houses.

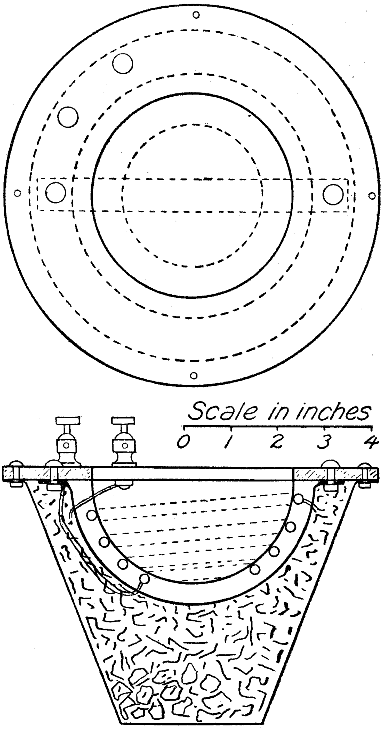

FIGURE 2.—Diagram of supporting case for electric heaters.

The type of heater just described is not necessarily the only one that can be used. More efficient and convenient types could undoubtedly be produced on a commercial scale and the authors have been advised that one concern, at least, is contemplating the manufacture of an electric heater adapted to this purpose.

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[4] Nonpareil bricks, made by the Armstrong Cork Co., Pittsburgh, Pa.

GAS HEATERS.

General experience has indicated the advisability of using electric heaters for the distillation of crude petroleum. However, these convenient devices are not universally available and accordingly some tests have been made to show that heating by gas is practicable. Some Pennsylvania oil was distilled both at atmospheric pressure and in vacuum for the purpose of comparing the usual type of electric heater and a Meker gas burner. The latter was selected from several possible types of gas burners because of its intensely hot flame. The assembly of the apparatus was the same as when an electric heater was used (see figure 9) except that the flask rested on a piece of $\frac{1}{4}$-inch transite board in which was cut a $3\frac{1}{2}$-inch circular hole. The burner was protected from air drafts by a suitable inclosing shield. In the authors' tests the burner was equipped with a supplementary needle valve for regulating accurately the flow of gas, which would have been unnecessary if the burner had had a built-in regulating valve. The flame was permitted to come directly in contact with the flask bottom, which was possibly unsafe, but inasmuch as the glass had a low coefficient of expansion the liability of breakage was believed to be moderate. The vapor temperature at both atmospheric and reduced pressure could be carried up to about 275° C. (527° F.), the usual maximum for an "air" distillation. By covering about half of the exposed part of the flask bulb with asbestos it was found possible to continue up to 300° C. (572° F.), which is the maximum usually desired in a vacuum distillation. Results of distillations of a given oil with gas and electric heating were identical within the usual limits of experimental error. Several Meker burners were tried and one of medium size, about 8 inches high and $1\frac{3}{16}$ inches in diameter at the top, proved the most satisfactory.

The authors realize that their experience with the method of gas heating it too limited to permit authoritative discussion of the subject. The information is merely offered to show that electric heaters are not absolutely essential in the analytical distillation of crude petroleum, either at atmospheric pressure or in vacuum.

DISTILLATION FLASK.

In Bulletin 125[5] of the Bureau of Mines a flask is described that permits the use of a fractionating column about $5\frac{1}{2}$ inches high by $\frac{7}{8}$ inch diameter. The distillation charge is 200 c. c. or less of oil. This

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[5] Rittman, W. F., and Dean, E. W., The analytical distillation of petroleum: Bull. 125, Bureau of Mines, 1916. p. 66.

flask proved satisfactory in service, but could not be obtained in the market, as no large manufacturer of glassware seemed willing to include it in his regular line, and flasks made to special order by small manufacturers were of poor quality. For a time the Pittsburgh Petroleum Laboratory used flasks handmade by the bureau glass-blower. But the bureau could not advise other laboratories as to a satisfactory source of supply, and accordingly a change was made when another slightly different type became available in the market. The form and dimensions of the No. 26 Pyrex distillation flask now in use are shown in figure 3. It is used with a charge of 300 c. c., or less, of oil and permits the use of a fractionating column about 6½ inches high and 1 inch in diameter. This type of flask undoubtedly has a slightly greater tendency to cause cracking of oil than the smaller flask previously used, but the tests showed that usually distillation at atmospheric pressure can be carried safely up to 275° C. (527° F.), and distillation at 40 mm. pressure up to 300° C. (572° F.)—points that are high enough for all ordinary needs. In many respects the larger flask seems preferable to the earlier type; it is easily obtainable, and is of excellent quality.

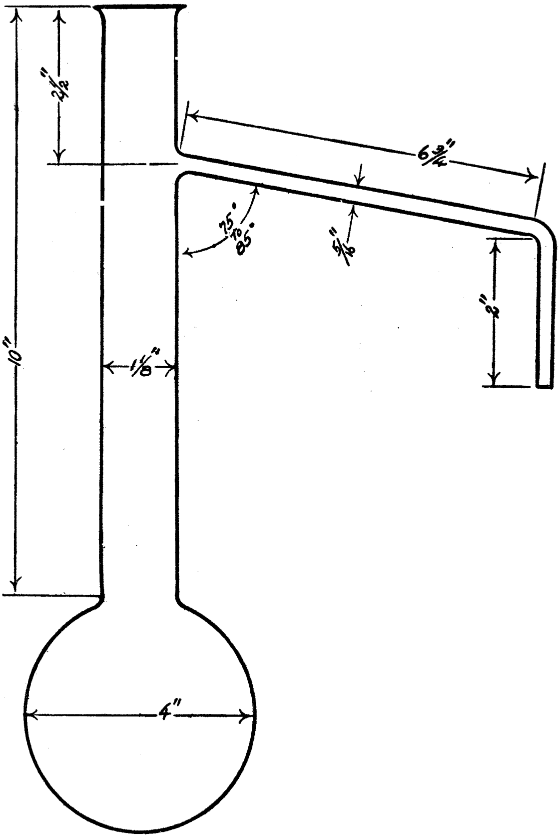

FIGURE 3.—Outside dimensions of 300-c. c. charge Hempel flask used by the Bureau of Mines.

FRACTIONATING COLUMN.

The fractionating column now generally used by the bureau is made of a length of iron "jack" chain of about No. 18 size, sufficient to pack under its own weight into a column 1 inch in diameter, and 6½ inches long. It is "strung" on a wire ring so that it hangs as a mass about a foot long, which makes the chain more convenient to handle than when it is not looped together.

The device used for supporting this column (see fig. 4) is made of a suitable length of wire, preferably though not necessarily nickel chromium, of about No. 18 gage. One end is wound in a spiral a little less than an inch in diameter and the remaining wire is bent at right angles to the plane of the spiral, and is cut off at a length of about 9½ inches. A small loop is bent into the end away from the spiral and is put through a hole drilled in a strip of spring steel or other suitable material about 0.015 inch thick, three-eighths inch wide, and 3 inches long which is bent around a cylinder 1 inch in diameter. When allowed to expand this spring strip holds firmly on the inside of the flask neck and provides a secure support for the column of chain.

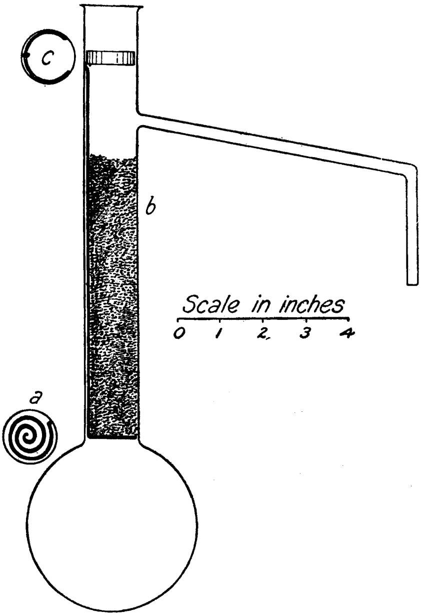

FIGURE 4.—Fractionating column and supporting device in a Hempel flask: *a*, Detail of wire spiral supporting fractionating column; *b*, fractionating column of iron "jack" chain; *c*, detail of spring clip that holds column in position.

In Bulletin 125 the use of aluminum beads was recommended for the fractionating column, but the iron chain is more readily obtainable in the market and is much easier to remove from the flask neck. Columns of iron chain and aluminum beads, when compared by distilling the same oil, have given results that were identical within the normal limits of error.

CONDENSER.

The authors have used and are using for the analytical distillation of crude petroleum several types of condensers that vary in details of construction but satisfy the following general requirements:

1. The tube in which oil vapor is condensed is practically vertical, which prevents "lag."

2. The tube, though designed to have a large area of cooling surface, is relatively short, about 16 to 18 inches over all, which avoids the necessity of having the distilling flask at a high elevation above the laboratory bench.

3. The condensing tube is designed so that it insures thorough contact of vapor with the cooling surface and thereby prevents "channeling" of uncondensed vapor.

4. The jacket surrounding the condenser tube is of a type that permits the use of a cooling medium of any desired temperature. Thus for the volatile distillates a mixture of ice and water is employed, whereas for very viscous distillates or for fractions containing appreciable quantities of crystalline paraffin wax the "cooling" medium may be water warmed to a temperature above the melting point of the wax.

5. The condenser jacket is constructed so that moisture can not condense on the outside and drip or flow down into tubes used for collecting the distillates. Sometimes this has been accomplished by insulated double-wall construction, and again by using a drain trough to catch any drops that may fall.

The type of condenser chiefly used by the authors is a glass tube with three-staggered ellipsoidal bulbs surrounded by the cooling jacket. The dimensions and general form of such a tube is indicated in figure 5. The over-all length is about 18 inches. At the top is five inches of five-eighths inch tubing, at the bottom six inches of seven-sixteenths inch tubing (both outside dimensions) with a diagonally ground tip. Each of the three bulbs is about 1¾ inches long and 1¼ inches in diameter. The bulbs are staggered so that parallel lines projected through the centers of the top and bottom tubes are about one inch apart.

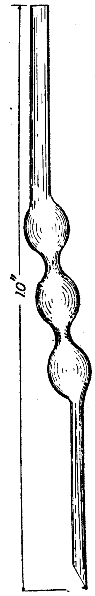

FIGURE 5.—Three-bulbed glass condenser.

The authors have successfully used tubes of Pyrex glass and of ordinary soft glass. The former are preferable, but the latter have given good service. The advantage of Pyrex is that its tendency to crack is slight when the vapor inside the tube is very hot and the jacket water very cold. This advantage is perhaps more theoretical than actual as only one or two soft glass tubes have cracked in the course of distillation tests during at least five years.

The bulbed tubes described above are moderately easy to make and are as durable as most of the ordinary pieces of laboratory glassware. They are, however, occasionally broken either in handling or in shipment and the authors have, therefore, developed a type of metal condenser tube that has recently been put in service and has proved very satisfactory. The dimensions and details of construction of this tube are indicated in figure 6. It consists of four parts, a top tube and cap, a large cooling tube with a smaller tube attached to the bottom, a filler, and a spiral rod. The construction is such that the vapors entering through the top tube are spread through the annular space between the large cooling tube and the filler which brings them in contact with a large area of condensing surface. The condensed liquid drains through the smaller tube attached at the bottom of the cooling tube. The spiral fits rather loosely but when wet with condensate seals across the annular space and causes the current of vapor to follow a spiral path which insures use of the entire cooling surface and eliminates the possibility of channeling. The filler is simply a piece of metal tubing of proper size with a conical cap and an open bottom. Three legs at the bottom prevent sealing off the bottom opening.

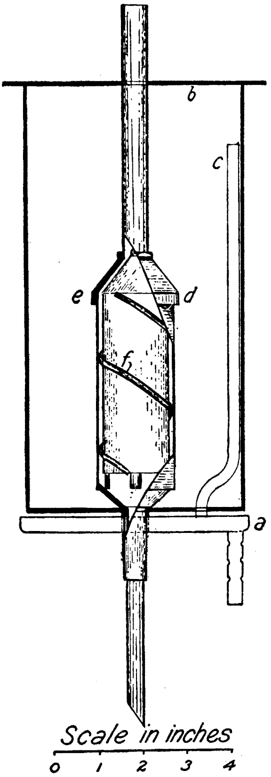

FIGURE 6.—Cooling jacket. *a*, Drain trough with outlet; *b*, bath with *c*, constant-level overflow tube; *d*, annular metal condenser tube with open-bottom, hollow filler and *f*, loosely fitting spiral; *e*, fiber gasket and screw joint connecting the two parts of the outer tube.

The cap holding the top tube and the main cooling tube is connected by a screw joint, made tight by a fiber gasket. The authors have used for this, as also for other parts described later, a special composition fiber sold under the trade name of "Janos." Other equally satisfactory materials are undoubtedly available in the market. The condenser can be easily opened and both its interior and the filler and spiral can be cleaned.

The cooling jackets used by the authors are essentially cylindrical containers about 10 inches deep and 4½ inches in diameter, inside dimensions. Two types have been used. One has double walls separated by a ½-inch layer of granular cork, which minimizes condensation of moisture on the outside of the jacket when the latter is filled with cracked ice and water. It gives satisfactory service but is rather difficult to construct, at least in the bureau instrument shop, which does not specialize in sheet metal work. A simpler type of condenser jacket, shown in figure 6, has only a single wall, but has a drain trough at the bottom that catches the "drip" and overflow and discharges through an outlet connecting with the sink.

RECEIVING TUBES.

In the work described in Bulletin 125 the percentages distilled were recorded in terms of weight, which has certain advantages but is subject to objection on the ground that commercial transactions in the United States are practically always in terms of volume. Accordingly, the practice of reporting in terms of weight has been discontinued and the volume system adopted. Ordinary graduated cylinders can be used to collect fractions but the authors prefer graduated test tubes such as are shown in figure 7.

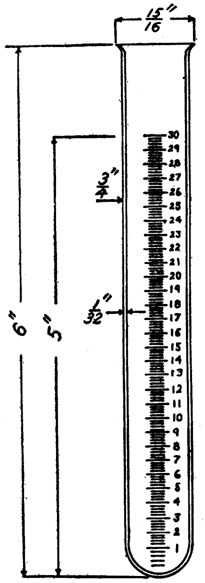

FIGURE 7.—Standard test tube for vacuum distillation.

THERMOMETER.

The problem of temperature measurement has been discussed in some detail in Bulletin 125. For the present work either of two methods may be followed:

1. Measuring actual temperatures;
2. Reporting results in terms of a reproducible system of thermometer readings.

The first method is theoretically desirable and is not prohibitively difficult, but it involves certain complications in procedure incommensurable with the advantages gained. The instruments regarded as most desirable are either thermoelectric devices of proper type or mercury thermometers for which so-called stem corrections have been accurately determined. The authors have always regarded the so-called "partial immersion" thermometer with a certain degree of distrust. Such thermometers are scaled by the makers to include the correction for cooling of the immergent stem, but there is no assurance that the temperature of this stem at the time of scaling is the same as that existing under conditions of actual use.

The Bureau of Mines favors for crude-oil distillation as well as for gasoline distillation the use of a thermometer of specified dimensions, calibrated for total immersion and used without correction for the cooling of the emergent stem. Specifying dimensions insures that readings shall always agree for different instruments used under the same conditions and the fact that results are actually expressed as thermometer readings rather than true temperatures is regarded as of little practical importance. Distillation results are little more than comparative under any conditions, and all that is desired is a reliably uniform system of temperature comparison.

The instrument recommended by the authors is the "A. S. T. M low-distillation" thermometer, adopted as a tentative standard by the American Society for Testing Materials in June, 1921, and covered by the following specification:

SPECIFICATIONS FOR A. S. T. M. THERMOMETER.

Type: Etched stem, glass.

Total length: 381 mm.

Stem: Plain front, enamel back, suitable thermometer tubing. Diameter 6 to 7 mm.

Bulb: Corning Normal, Jena 16 III, or equally suitable thermometric glass. Length, 10 to 15 mm.; diameter 5 to 6 mm.

Actuating liquid: Mercury.

Range: 0° C., or 30° F., to 300° C., or 580° F.

Immersion: Total.

Distance to 0° C., or 30° F., mark from bottom of bulb: 100 to 110 mm.

Distance to 300° C., or 580° F., mark from top of stem: 30 to 45 mm.

Filled: Nitrogen gas.

Top finish: Glass ring.

Graduating: All lines, figures, and letters clear cut and distinct. Scale graduated in 1° C. or 2° F. divisions and numbered every 10° C. or 20° F., every fifth graduation being longer than the others.

Special markings: "A. S. T. M. Low Distillation," serial number and manufacturer's trademark etched on the stem.

Accuracy: Error at any point on scale shall not exceed one-half smallest scale division.

Test for permanency of range: After being subjected to a temperature of 290° C. or 560° F. for 24 hours the accuracy shall be within the limit specified.

Points to be tested for certification: 0°, 100°, 200°, 300° C. or 32°, 212°, 400°, 570° F.

PROCEDURE.

FILLING FLASK.

Measure 300 c. c. of oil into the distilling flask. If a sample of 300 c. c. is not available a smaller charge can be used, but not less than 200 c. c. should be used for reasonably accurate results. For the less viscous types of crude oil a pipette or graduate may be used. Decidedly viscous oils can be handled in a pipette if suitable precautions are taken. The pipette should not be drawn to a point and the oil may be drawn in by mechanical suction and expelled under air pressure. Drainage can be completed by warming the pipette gently with a luminous gas flame, if care is taken not to ignite the charge of oil nor to boil or carbonize the oil residue in the pipette. The dimensions and form of a 300-c. c. pipette are shown in figure 8. Sometimes weighing the charge of oil is more convenient than measuring it. The specific gravity of the oil is first determined and the weight in grams of 300 c. c. is calculated. The weight in grams of 300 c. c. of oil equals 300 times its specific gravity. This quantity is weighed in conveniently by the use of a pipette from which oil can be discharged or with which oil can be withdrawn until the desired amount is placed in the tared flask. After the correct volume of oil is in the flask a boiling stone, a bit of unglazed porcelain, or other porous material, is dropped in.

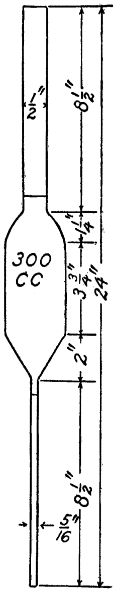

FIGURE 8.—Pipette for measuring distillation charges of crude petroleum.

ADJUSTING FRACTIONATING COLUMN.

The supporting device for the fractionating column is slipped in place so that the spiral is about on a level with the point at which the flask neck starts to widen out into the bulb. The column of iron chain or aluminum beads is then put in position. The filling material can be packed and made to fill the entire space by tapping while putting it in place, but the column can not be compressed after the material is in. The column should come to 1 inch to 1¼ inches of the lower level of the side tube.

ADJUSTING THERMOMETER.

The thermometer is passed through a cork stopper that has been bored to fit its stem. The cork should be rolled till thoroughly softened before it is bored to fit the thermometer; also heating and slightly charring its surface helps to smooth and soften the cork and cures it of any tendency to swell and put the flask neck under strain during the distillation. A thin film of 3 to 5 mg. of long-fibered absorbent cotton is twisted on the bulb of the thermometer. The thermometer should be placed so that the top of the bulb is about one-sixteenth inch below the lower level of the side tube to insure the whole bulb's being in the current of vapor.

SETTING UP APPARATUS.

Figure 9 shows the apparatus set up for use. The condenser jacket is filled with a mixture of cracked ice and water, not cracked ice alone. The flask is placed on the electric heater, or supporting asbestos board if a gas burner is used, and is connected by means of a carefully fitted cork stopper, with the condenser tube. The receiving graduate is placed under the condenser tube in such a position that the latter projects downward into it for at least an inch. For the first three or four fractions the receiving tube ought to be surrounded by cracked ice and water. Place two or three of the graduated test tubes in a beaker filled with the cooling mixture, and set the beaker on a wooden block high enough to bring the test tubes an inch or so up around the condenser tube. To change the receiver take the beaker in one hand, remove the block for a moment, lower the beaker, and slip a second receiving tube under the condenser tube. Then return the wooden block to its original position. This change can usually be accomplished without losing a single drop of distillate.

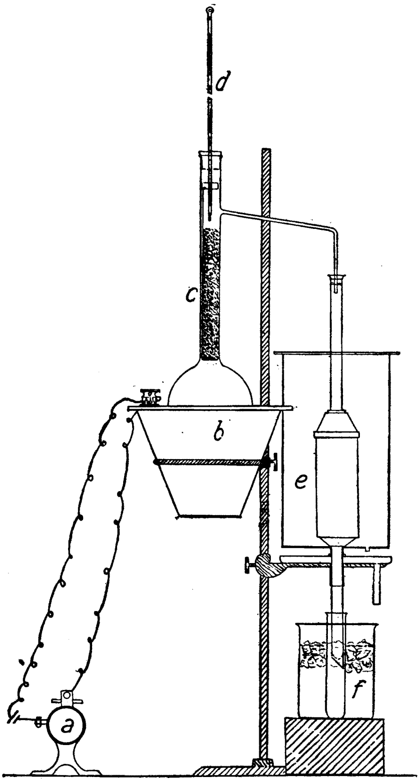

FIGURE 9.—Apparatus assembled for distillation of crude petroleum. *a*, Rheostat for regulating current passing through electric heater; *b*, electric heater; *c*, flask with charge of oil and fractionating column; *d*, thermometer; *e*, condenser; *f*, receiving graduate in beaker of ice water supported by wooden block.

After the apparatus has been set up both corks should be luted with a thick paste of litharge and glycerin. These two materials are kept separately in stoppered containers until the paste is needed, when they are mixed and applied with a small stiff-bristled brush. If the materials are sufficiently free from water the paste sets in a few minutes to a dense hard mass. Satisfactory results have been obtained with a material sold as "glassmakers" litharge, for which no preliminary dehydration seems necessary. If a doubtful grade of litharge must be used it can be ground in a mortar to pass a 100-mesh screen and dried for an hour at a temperature of 350 to 400° C. (622 to 752° F.3. Commercial glycerin has proved satisfactory, but it should be kept properly stoppered to prevent its absorbing moisture from the air.

CONDUCTING DISTILLATION.

After the apparatus is set up heat is applied and the distillation started. Due to the presence of the fractionating column some little time elapses between the time when the liquid starts to boil and the time when the vapor comes into the condenser. On this account heating can be vigorous at first and then reduced as soon as boiling begins. There is no objection, of course, to heating up the charge of oil slowly, provided it is not necessary to save time.

After the distillation has begun the heat is regulated so that the oil comes over at a rate of from 1 to 3 drops a second. Two drops a second is preferred. The temperature is read when the first drop falls from the end of the condenser. A fraction is separated at every temperature point, above the first drop temperature, that is a multiple of 25° C. If a Fahrenheit thermometer is used the cut limits should be temperatures equivalent to multiples of 25° C., as for example, 122° F., 167° F., 212° F., etc. The volume of each fraction is read and recorded as soon as possible after separation and the fraction is immediately corked and set aside for further examination, such as measurement of specific gravity.

The distillation is usually continued until a vapor temperature of 275° C. (527° F.) is reached. Certain oils, such as those from Pennsylvania, can often be carried safely to 300° C. (572° F.) or higher, but Mid-Continent and Western oils frequently start to crack between 275° C. (527° F.) and 300° C. (572° F.). Cracking is evidenced by a copious flow of distillate with a thermometer reading that advances very slowly or may even remain stationary or slightly recede. Some oils have been known to crack between 250° C. (482° F.) and 275° C. (527° F.), but the latter is usually a safe limit.

Samples of crude petroleum may contain varying amounts of water unless they are previously dehydrated. If viscous crudes contain even a trace of water they froth and are practically impossible to distill by the method given unless subjected to previous treatment. (See p. 65.) Less viscous crudes that contain not more than 1 per cent of water can frequently be distilled directly until all water has been swept out of the Hempel flask, as evidenced by the disappearance of droplets of moisture condensed on its walls. When the water is all gone the distillation is stopped and the flask allowed to cool; the thermometer is removed and the distillate, which has been separated from the water, is poured back; the thermometer is then replaced and the distillation started again. In calculating results allowance is made for whatever percentages of water the oil contained. Thus, if 2 c. c. of water are found the percentage results are calculated by dividing the volume of the various fractions by 2.98 instead of 3.

If the water content of a nonviscous crude oil is of the order of 0.1 per cent or less it is generally unnecessary to resort to the procedure of stopping the distillation, cooling and pouring back the distillate, as results are not appreciably affected by this proportion of water in the vapor. If notably more than 1 per cent is present, the Hempel column may not prevent drops of water from falling back into the boiling oil, which, if the oil were much above 100° C. (212° F.), would cause a miniature explosion that might blow the filling material and thermometer out of the flask.

A second source of trouble is "flooding," which sometimes occurs at temperatures above 225° C. (437° F.). The dimensions of the flask and fractionating column recommended by the bureau have been chosen, so that ordinarily no tendency to flood occurs below a vapor temperature of 300° C. (572° F.). Occasionally, however, the oil condensed in the fractionating column does not drain back into the flask readily enough, but accumulates in the neck of the flask and may go over into the condenser. This trouble can be remedied by turning off the heat long enough to let the liquid drain back into the bulb of the flask and then placing a shield of asbestos paper or other suitable insulating material around the flask neck to cut down the condensation in the column.

INTERPRETATION OF RESULTS.

The data regarding the agreement of laboratory and plant results are not as comprehensive as might be desired. However, the results of the present distillation method show definitely that it can be used to determine the content of gasoline. The present Government specifications for gasoline require that the 90 per cent distillation mark be not higher than 190° C. (374° F.) and that the end point be not higher than 225° C. (437° F.).

Table 3.—*Distillation range in the A. S. T. M. apparatus of fractions distilled from crude oils by the Bureau of Mines Hempel method.*

	Fractions cut at 175° C. (347° F.).				Fractions cut at 200° C. (392° F.).	
	A.[a]		B.[b]		C.[c]	
	°C.	°F.	°C.	°F.	°C.	°F.
First drop	73	163	61	142	63	145
10 per cent	104	219	92	198	95	203
20 per cent	111	232	99	210	106	223
30 per cent	113	235	106	223	116	241
40 per cent	127	261	113	235	126	259
50 per cent	134	273	120	248	136	277
60 per cent	140	284	127	261	145	293
70 per cent	147	297	136	277	156	313
80 per cent	155	311	146	295	167	333
90 per cent	165	329	160	320	182	360
95 per cent[d]	175	347	173	343	200	392
End point	188	370	187	369	209	408

[a] Sample A represented 12.8 per cent of the crude distilled.
[b] Sample B represented 27.9 per cent of the crude distilled.
[c] Sample C represented 25 per cent of the crude distilled.
[d] Note that the 95 per cent mark is practically identical with the cut limit at the top of the respective columns.

Figures appearing in Table 3 show that the fraction distilling below 200° C. (392° F.) in the Hempel apparatus is not of higher end point than a commercial gasoline satisfying the present Government specification or even a more rigid specification. A fraction cut at 175° C. (347° F.) corresponds to a moderately "high test" commercial gasoline. Some of the lower points in the distillation curves of the fractions represented in Table 3 do not satisfy Government specifications but this undoubtedly could be corrected in commercial practice by the addition of 5 to 10 per cent of natural-gas gasoline. On the basis of these data no objection could be raised to the practice of considering the gasoline content of a crude oil as at least equal to the percentage distilling below 200° C. (392° F.) in the Bureau of Mines Hempel apparatus.

As regards the kerosene fraction, the authors lack conclusive information. Kerosene is not made to conform to a distillation specification but rather to satisfy requirements that concern chiefly its behavior in a wick burner. The fraction distilling between 200° C. (392° F.) and 275° C. (527° F.) is probably not greater than the yield of kerosene that might be obtained in good refinery practice. Lacking better evidence this assumption has been tentatively assumed and the results of a distillation at atmospheric pressure in the Bureau of Mines Hempel apparatus are interpreted as follows:

Fraction distilling below 200° C. (392° F.): Gasoline and naphtha.
Fraction distilling 200° C. (392° F.) to 275° C. (527° F.): Kerosene.
Fraction distilling above 275° C. (527° F.): Fuel oil and lubricating oil.

ROUTINE DISTILLATION OF CRUDE OIL IN A VACUUM.

GENERAL CONSIDERATIONS.

The separation of the residue boiling above 275° C. (527° F.) or 300° C. (572° F.) into further fractions of various ranges of volatility can be done without cracking either by a steam or a vacuum distillation. Distillation in the presence of a current of open steam is almost universally used in commercial refining and is used frequently in the laboratory. In connection with a quantitative analytical method, however, there are numerous complications and it seems preferable to use the scheme of vacuum distillation. Either of these methods accomplishes the same fundamental purpose of reducing the boiling point of the oil. Boiling occurs when the vapor pressure of the oil slightly exceeds the pressure of the atmosphere above it. The temperature at which a liquid boils can be lowered either by balancing part of this atmospheric pressure with the vapor pressure of a current of steam, or by reducing the atmospheric pressure by means of an evacuating pump. The latter method permits easier control and is more suitable in the laboratory. As steam is cheaper and easier to control on a large scale and is regarded as a little more effective in preventing cracking, it is preferred in plant operation.

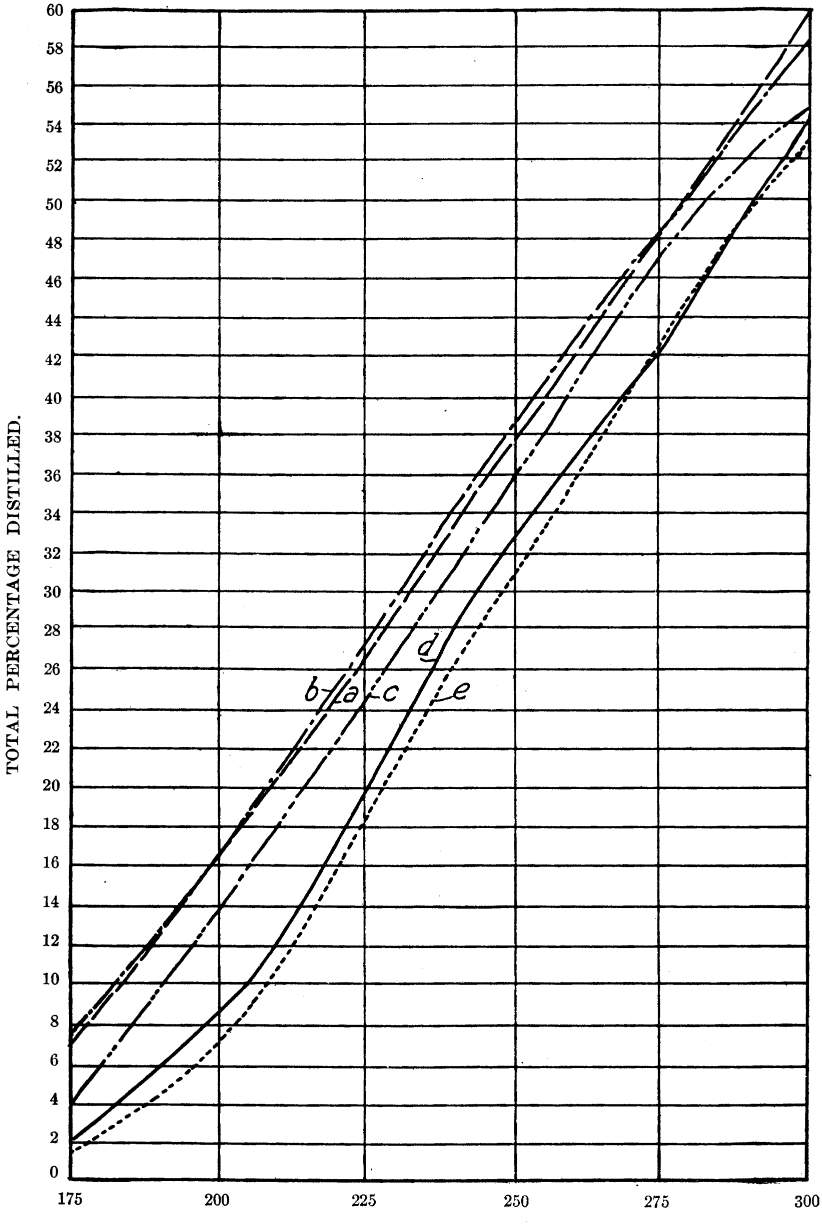

FIGURE 10.—Distillation curves for a sample of crude-oil residuum distilled at: *a*, 20 mm.; *b*, 15 mm.; *c*, 30 mm.; *d*, 40 mm.; and *e*, 50 mm.

In developing a method of vacuum distillation it was regarded as essential to employ the same flask as in distillation at atmospheric pressure, thus avoiding complications involved through transferring the residuum to another container.

A standard pressure for use in all tests was chosen. Common practice in many laboratories has been to work at whatever pressure the available vacuum pump happened to be capable of maintaining. As a result vacuum distillation figures are given for a variety of pressures and no data are furnished that permit translating results obtained at one pressure into terms of results obtained at another pressure. Therefore the use of one definite pressure that can be attained without too much difficulty seems advisable. A series of trial distillations were made with the same oil at pressures ranging from 15 mm. to 50 mm., results of which are shown in figure 10. Curves *a* and *b* are each averages of four tests, curve *c* of three, and curve *d* of two.

No startling differences appear in the results obtained at different pressures and the total percentages distilling below the various temperature limits, particularly the higher marks, are only moderately greater at 15 mm. than at 50 mm. Working at 15 or even 20 mm. is tolerably difficult unless a very efficient pump is used and the distillation system is maintained free from all but minute leaks. A pressure of 40 mm. can be maintained by any reasonably good mechanical pump or even by a water aspirator. The total amount distilling at this pressure up to 300° C. (572° F.) was found to be about 90 per cent of the amount distilling at 15 mm. and the greater ease in operation more than overbalanced this slight disadvantage. The bureau has, therefore, adopted as standard for vacuum distillations a pressure of 40 mm. and recommends this mark for practically all petroleum work.

APPARATUS.

HEATING EQUIPMENT.

The heating equipment, the distillation flask, and the thermometer used for vacuum distillation are the same as those used for distillation at atmospheric pressure.

SPRAY CATCHER.

One of the first difficulties encountered in attempting to distill high-boiling petroleum products in vacuum is a tendency for liquid oil to be blown over as a spray into the condenser. Bubbling is much more noticeable in distilling oil in vacuum than in distilling at atmospheric pressure, and the resulting spray must be trapped and separated from the vapor. The authors have found it possible to accomplish the desired result by means of a very simple mechanical device consisting of three cones of wire gauze placed in the neck of the distillation flask. These cones can be made in many ways. The following is recommended: The gauze, preferably brass or nickel-chromium of about 14 to 20 mesh, is pressed down over a wooden conical form 1 inch in diameter at the base and 2 inches high. An outside conical form fits over the wooden core. The meshes of the gauze are distorted, but the cones made in this way are uniform in dimensions, are seamless, and work satisfactorily. One cone is pushed down to the base of the flask neck, and two others are set about a quarter of an inch apart in the upper part of the flask neck with the rim of the upper cone about an inch below the side neck tube, as shown in figure 11, where the two top cones are close together.

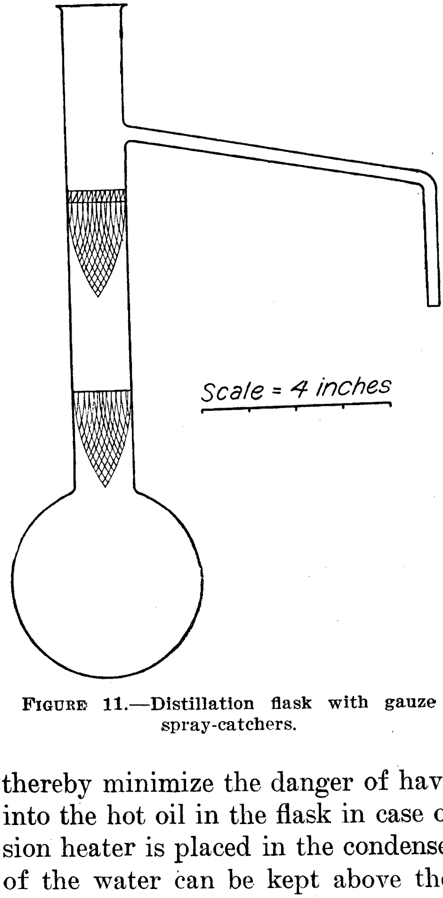

FIGURE 11.—Distillation flask with gauze spray-catchers.

CONDENSER.

Either type of condenser described on page 10 is satisfactory for vacuum distillations. The annular metal type has been used recently with slightly better results than the glass-bulb type. The latter, however, has been used widely in the past and is apparently as satisfactory for vacuum distillation as for distillation at atmospheric pressure. For vacuum distillation, Pyrex glass tubes are preferred to soft glass, as they are less liable to crack and thereby minimize the danger of having condenser water drawn back into the hot oil in the flask in case of breakage. An electric immersion heater is placed in the condenser jacket so that the temperature of the water can be kept above the melting point of paraffin wax which may otherwise tend to solidify and clog the condenser. Warm condenser water also decreases the viscosity of the distillates and reduces "lag." A temperature of 60° C. (140° F.) is recommended.

RECEIVING SYSTEM.

A vacuum distillation may be made to determine the percentages boiling between certain limits or to separate the various fractions for study. For the former a simple graduated cylinder attached to the condenser tube by means of a rubber stopper and connected with the line to the pump may be the receiver. The connection should preferably be a side tube sealed to the graduate, but a glass tube passing through the rubber stopper will be sufficient. A 100-c. c. graduate can ordinarily hold the vacuum fractions from an original charge of 300 c. c. of crude oil.

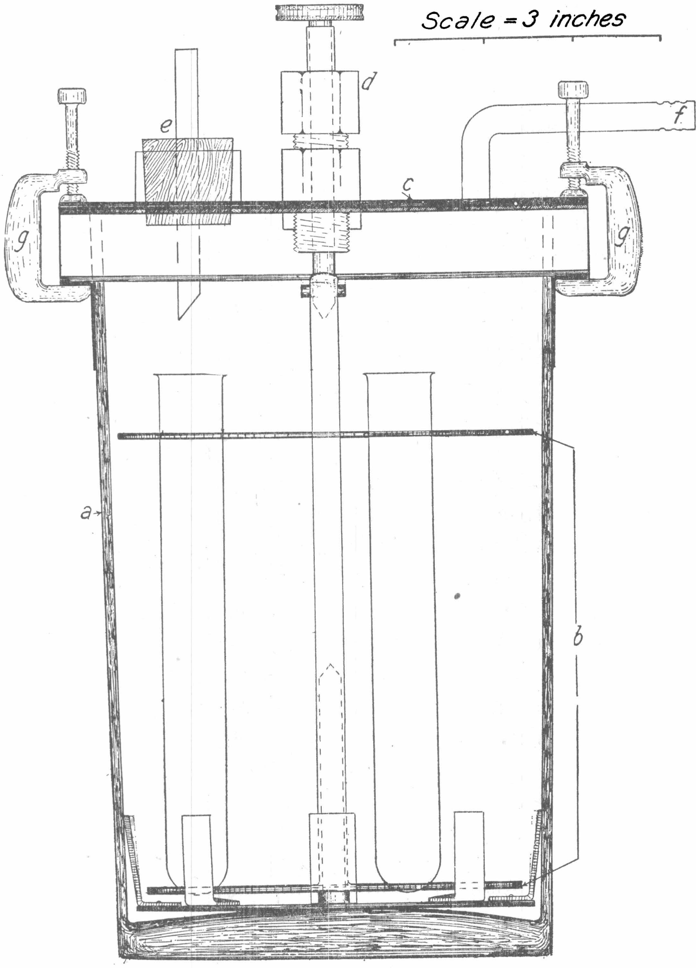

FIGURE 12.—Bruhl receiver used in distillation of petroleum. *a*, Glass jar; *b*, rotating metal rack holding graduated test tubes; *c*, metal top seating on glass jar with rubber gasket between; *d*, rod with knurled disk for rotating the rack; *e*, inlet for condenser tube through rubber stopper; *f*, tube connecting with manometer, pump, etc.; *g*, clamps holding lid on jar.

If fractions are to be separated, a more complicated receiving system must be used. A number of devices for this purpose have been described,[6] of which the Bruhl type seems preferable for handling relatively many small cuts. The authors have developed a Bruhl receiver, shown in figure 12, which is decidedly more satisfactory than the conventional models. The most important improvements are the elimination of leaky joints and the entry of the condenser tube through the top instead of through the side of the receiver.

This apparatus consists of a glass museum or specimen jar approximately 8 inches high without lid and with an inside diameter of 5 inches.

The exact size, however, is immaterial. The lid with its various accessories and the revolving rack for graduated test tubes are specially constructed of metal. The lid seats on a rubber gasket which is placed on the ground rim of the glass jar and is generally lubricated with castor oil. Four "draftsman's" clamps hold the lid down. These are unnecessary after a vacuum is established where the suction holds the lid down tight enough. The condenser tube projects a little below the lower surface of the lid and should clear the test tubes in the rack by about one-fourth of an inch. Various tests tubes can be brought in place under the condenser by revolving the rack by means of a rod with a knurled disk that projects through the stuffing box and engages with the center rod of the rotating rack. The condenser and the lid should be held in place by clamps and holding devices attached to a vertical iron support. The jar is set upon a block of wood about one inch thick, and can be removed from the lid by withdrawing the wooden block and lowering the jar to clear the various projections on the under side of the lid. The receivers used by the Bureau of Mines are designed to hold nine graduated test tubes of about 30 c. c. capacity. When smaller tubes are used, they are centered in the proper holes in the rack by means of small flanged metal adapters.

VACUUM REGULATING SYSTEM.

Success in making a vacuum distillation necessitates accurate control of pressure, uniformity being the important consideration. For instance, if the same oil were distilled respectively at 39 and 41 mm. the results would be identical within the usual limits of experimental error. If, however, during a distillation that was started at 40 mm. the pressure fell more than momentarily to 39 mm., uncontrollably rapid boiling would occur and the test would probably be spoiled. An increase in pressure to 41 mm. would stop boiling completely.

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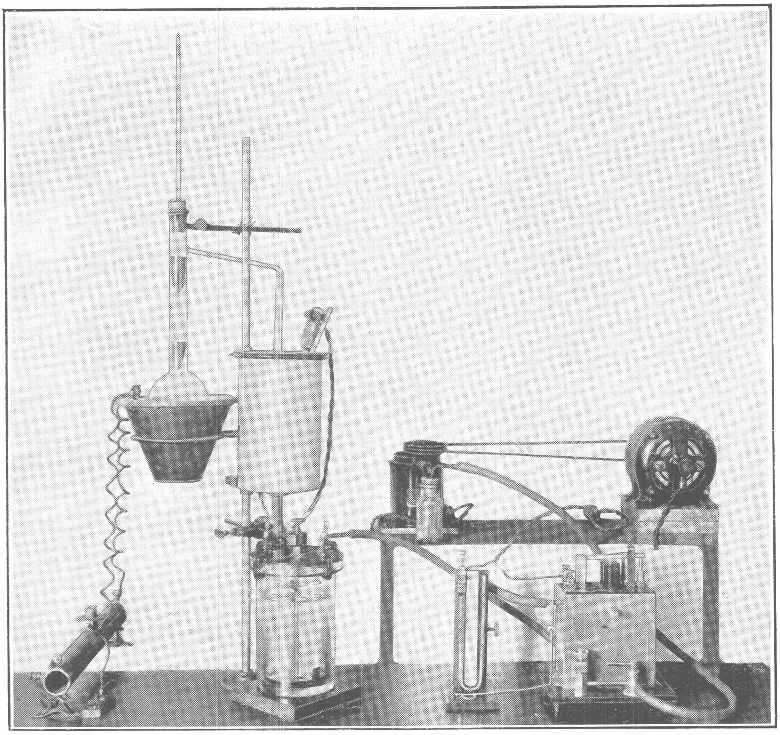
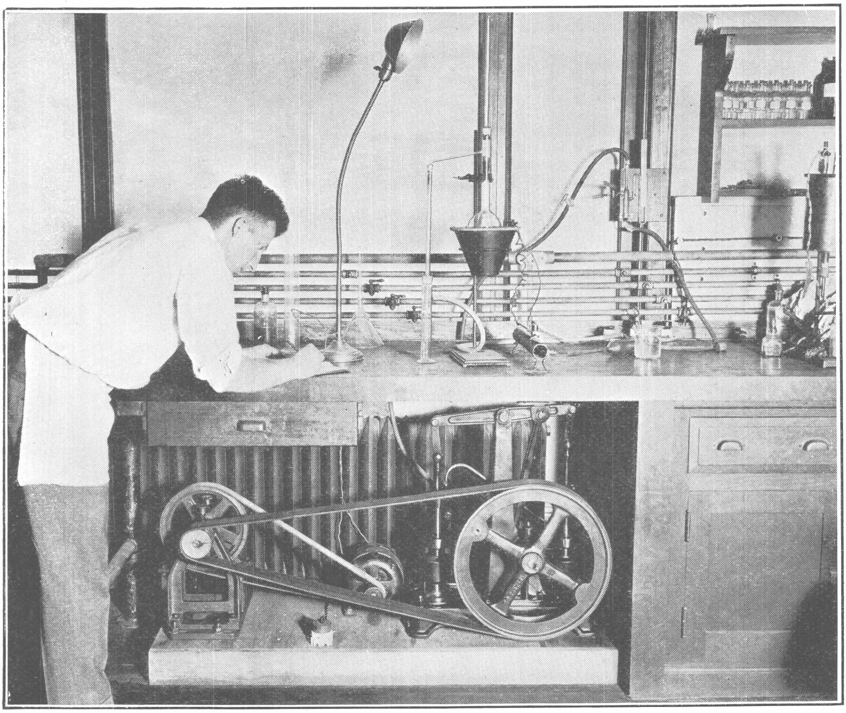
[6] Gatterman, Ludwig, Practical methods of organic chemistry, 2d American translation from 4th German edition, 1911, pp. 27–30. Young, Sydney, Fractional distillation, 1903, pp. 18–20.



A. APPARATUS FOR ROUTINE DISTILLATION OF CRUDE OIL IN A VACUUM.



B. EARLY APPARATUS USED FOR VACUUM DISTILLATION OF LUBRICATING OIL.

The several vacuum pumps used by the authors were able to maintain a pressure lower than 40 mm. and several schemes were devised to reduce their efficiency to the desired degree. The earliest and crudest procedure was to equip the line connecting the vacuum pump with the distillation system with a glass stopcock and a "bleed-in" T consisting of a fine capillary tube opening to the line through a glass stopcock. This equipment, shown in Plate I, *B*, is one of the earlier sets of apparatus used by the authors for vacuum distillation of lubricating oil. It was regulated by part "throttling off" the pump by means of the first-mentioned stopcock as a "course adjustment," and by opening the "bleed-in" stopcock as a "fine adjustment." This procedure obviously was not altogether satisfactory, as glass stopcocks are not adapted to the accurate metering of small orifices. The simple equipment described was, however, used for a considerable period of time and in the hands of experienced operators served its purpose fairly well. The "bleed-in" stopcock was equipped with a long wooden handle that increased the accuracy of control of the size of the orifice.

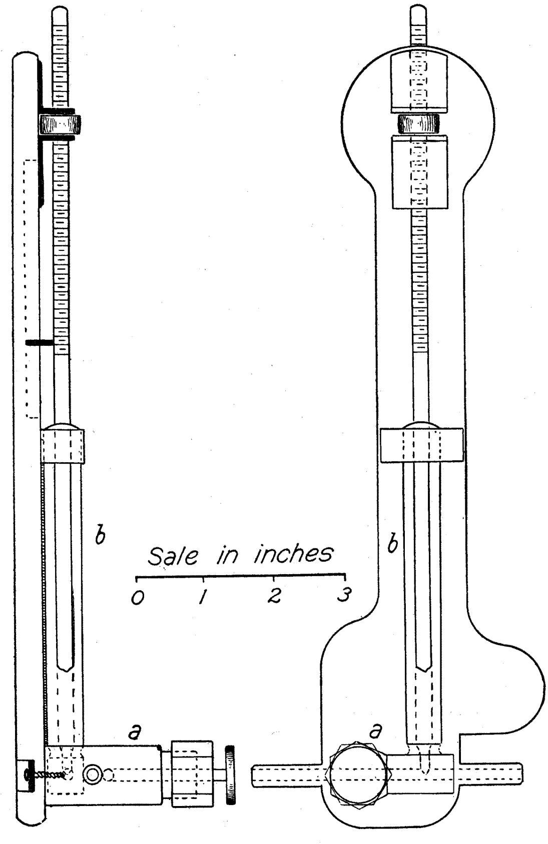


FIGURE 13.—Plan and section of sleeve-valve vacuum regulator; *a*, throttling valve with tube to vacuum pump on one side and tube to manometer and distillation system on the other; *b*, sleeve valve opening into the tube that connects valve *a* with the distillation system.

The first improvement was made by substituting a sensitive metal needle-valve for the "throttling" glass cock, and replacing the "bleed-in" stopcock by a device that was, in effect, a capillary tube of adjustable length. It consisted of a brass barrel with a plunger that had just enough clearance to let a small amount of air leak through. The length of the "capillary" that controlled the rate of flow of air into the evacuated system depended on the distance the plunger entered the barrel. The plunger was equipped with a screw device that permitted accurate control of its position. Figure 13 shows the construction. The sleeve-valve vacuum regulator, although satisfactory, was later replaced by an automatic control system.

AUTOMATIC VACUUM CONTROL.

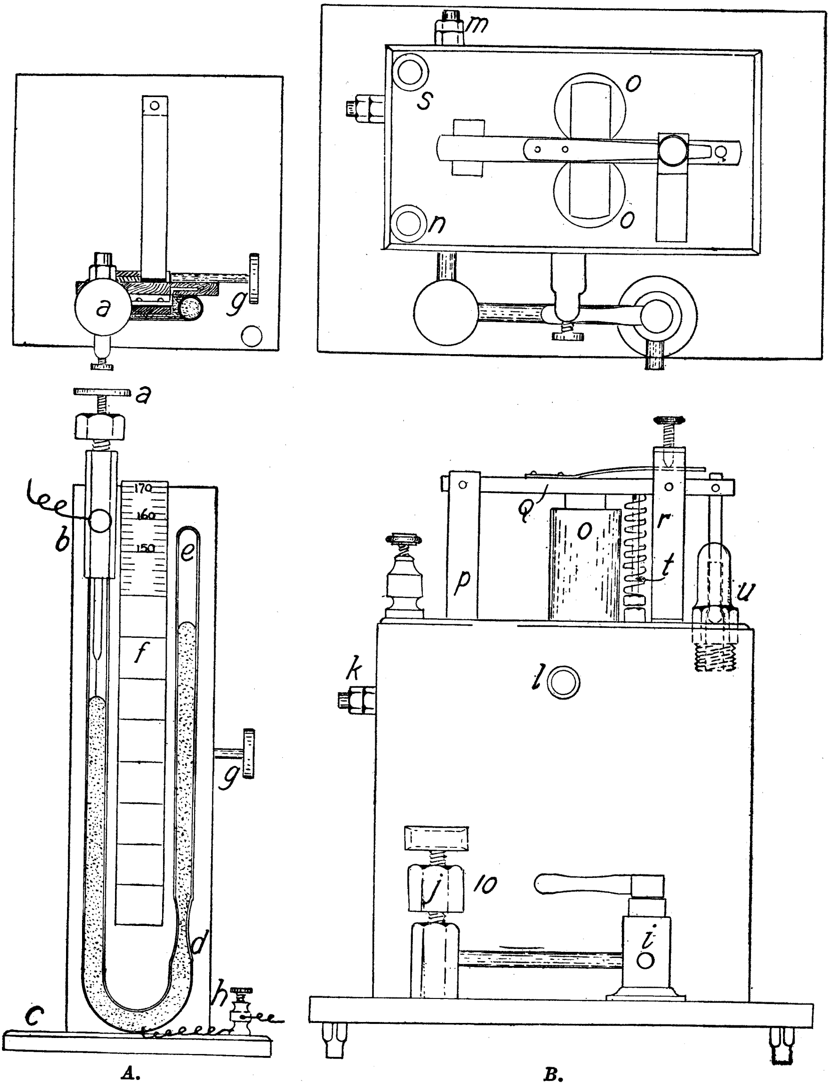
The advantages of automatic control of pressure for vacuum distillations were early recognized and many attempts have been made to design a satisfactory instrument of this type. One regulator that was constructed and tried consisted of a "bleed-in" valve operated by the movement of a copper bellows connected with the control system. This type of regulator is still believed to be workable, but the one actually constructed proved unreliable and difficult to adjust.

The automatic regulator now in use (fig. 14) consists essentially of a mercury manometer with platinum contact points closing a low voltage circuit when the desired pressure is reached, and a "bleed-in" valve operated by an electromagnet that is excited when the mercury touches the platinum point.

The manometer and valve were soon discovered to be seriously irregular in action except when a moderate sized reservoir was connected with the system. The regulating system now in use is built around the reservoir, which simplifies the mechanical problem of finding places for the various valves and connections.

The "bleed-in" valve is of the poppet type, seating from the inside rather than the outside of the system. The difference in pressure helps the valve to open and prevents "sticking" when closed. The magnetic actuating mechanism is of the vibrating type and prevents any tendency the valve might have to stick while open. When the mercury of the manometer closes the circuit the valve, in opening, promptly breaks it, the principle involved being that of the ordinary electric bell or buzzer. This method permits a very delicate adjustment of the rate of flow of air through the valve as the period of vibration can be regulated accurately by a screw touching a spring contact.

The authors have used two of these automatic regulating devices. The first was crude in appearance and the manometer was not satisfactory. It was extensively used, however, and is still in good working order. The second set, which is shown in figure 14, is identical in principle but of better mechanical design. The manometer is adjusted so that the circuit is closed when the desired pressure (generally 40 mm.) is attained. This can be done in either of two ways. The first manometer used had two platinum contacts sealed in the glass, and adjustment was made by changing the quantity of mer-



A. *B.*

FIGURE 14.—Plan and section of automatic vacuum regulator. *A*. Regulating and indicating manometer—*a* and *b*, connection on open arm of manometer, including opening to regulating system, binding post, and stuffing box through which passes a rod bearing a platinum contact point; *d* and *e*, glass manometer tube attached to metal collar at *b*, with sealed-in platinum contact at *c*, constricted to about 1 mm. internal diameter at *d*, and closed end at *e*; *g*, knurled head operating rack and pinion which moves indicating scale *f*; *h*, binding post connecting with platinum contact at *c*. *B*. Regulator consisting of magnetic inlet valve, pressure stabilizing chamber, valves, and other accessories—*i*, shut-off valve in line connecting with vacuum pump; *j*, needle valve used as a coarse adjustment to "throttle down" line to pump; *k*, connection for rubber tube passing to *a*; *l*, auxiliary inlet valve by means of which system can be opened at end of a distillation; *m*, nipple for rubber tube connecting with receiver of distillation system; *n*, binding posts for electrical connections in circuit operating magnetic valve; *o*, magnet coils; *p*, post supporting moving arm of valve mechanism; *q*, moving arm of valve mechanism with supplementary spring for electrical contact; *r*, post with adjustable screw contact which touches spring on moving arm; *s*, binding post; *t*, spiral spring pushing up on moving arm and tending to keep inlet valve closed; *u*, inlet valve which is opened when magnet, *o*, is excited by closing of circuit in manometer *A*. NOTE.—Electrical circuit is as follows: Source of 10–12 volt direct current, to *a* to *c* to *h* to *n*, through *o*, through *p*, through *q*, through *r* to *s* to source of current.

cury in the tube by the use of a capillary pipette that entered through a stopcock sealed on the open arm of the manometer. The more recent type of manometer, shown in figure 14, has a movable platinum contact and can be adjusted by a knurled head and screw.

When the contacts have been adjusted the throttling valve is opened and the pump started. After the desired pressure has been reached and the automatic valve has commenced to act, the throttling valve is turned back until contacts occur only once every three or four seconds, after which the vacuum system needs no further attention except to note that the valve keeps on vibrating periodically. However, adjustment of the screw of the make-and-break contact so that the period of vibration is as rapid as possible is recommended, as it seems to give a more sensitive control of the rate of inflow of air than with slower vibration.

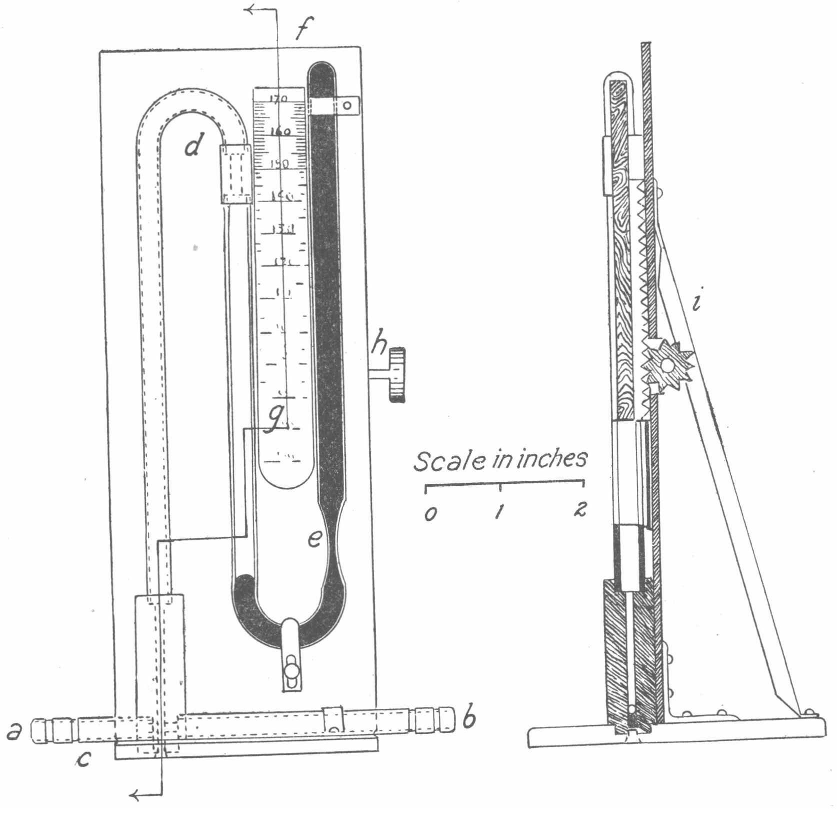


FIGURE 15.—Design of indicating manometer used by the Bureau of Mines. *a–b,* Metal tube in line from pump and regulating device to distillation system; *c–d,* metal tube and connecting pieces attached to line *a–b,* at one end and holding glass manometer tube; *d–f,* filled with mercury and constricted to about 1 mm. internal diameter at *e; g,* scale for reading pressures; *h,* knurled head for adjusting position of scale; *i,* rack and pinion by means of which the scale adjustment operates.

MANOMETER FOR USE WITH NONAUTOMATIC REGULATOR.

The type of manometer shown in figure 14 has proved so convenient that several of the principles involved were applied to the design of a simple indicating manometer used with the nonautomatic regulator and also for any other work requiring measurement of vacuum. The important details are a mounting in which connections and adjustments are made on metal parts, thereby avoiding placing the glass under strain; a rack and pinion for adjusting the measuring scale; and method of mounting the glass U tube which permits shipping a filled manometer without danger of its being spoiled. The construction of the manometer is shown in figure 15. The glass tube containing the mercury is connected with the metal tube by cementing it into the sleeve provided. De Khotinsky cement is recommended.

Filled manometer tubes can be shipped without damage by making the arm connecting with the metal sleeve overlength and filling the tube in the usual manner by evacuating and boiling out. The mercury is allowed to fill the glass completely up to almost the top of a capillary point on the overlength arm. This capillary is then sealed off in the flame. The resulting tube has only a small bubble of air which is held so firmly in place that the tube can be shaken violently in all positions without danger of the bubble going over into the other arm. The constriction in the closed arm of the manometer also helps to prevent displacement of the mercury by air. When a manometer is to be put in use the tip of the capillary can be broken off and the excess mercury removed with a pipette of small bore. The glass is then cut off at the proper mark and cemented into the sleeve on the metal tube of the stand, after which the assembled tube is attached to the stand.

PUMP FOR MAINTAINING VACUUM.

A pressure of 40 mm. can often be maintained by the use of a good water aspirator. Such a pump, however, is not recommended unless variations, when the water-pressure changes, can be controlled.

The authors have run distillations successfully with a water aspirator, but regard a mechanical pump as much preferable.

A two-cylinder pump of the Geryck type (Pl. I, *B*, see p. 24), driven by a one-fourth h. p. electric motor through a set of speed-reducing pulleys has been much used by the Bureau of Mines. The pump is heavy and the installation is both bulky and expensive; however, it has a high operating capacity—it can hold a vacuum of 5 mm. or less—and it is absolutely reliable. The bureau's pump has never required adjustment or repair during about five years' service. A little oil is put in the cylinders occasionally, otherwise the pump has needed no attention. The authors do not recommend that laboratories buy this type of pump, but if one is in stock and space is available its use is recommended. A one-fourth h. p. motor can drive it and the speed-reducing pulleys should be in such ratio that the fly wheel of the pump makes 60 to 80 r. p. m.

The Nelson type of pump, which is cheap, compact and efficient, has also given good results in the bureau laboratories. The ones used by the authors are driven by one-eighth h. p. motors, the pulley ratio being such that the pump is turned about 800 r. p. m. These pumps are of the two-stage type and have proved capable of maintaining a vacuum of 10 to 18 mm. under the conditions involved in the distillation test. This gives an ample margin under the usual working pressure of 40 mm. and after a distillation starts the throttling valve needs to be only slightly open. The gears of the pump run in oil, which tends to bubble out and spatter from the pulley. Therefore the pump should be protected with a shield. A satisfactory grade of oil for this type of pump has a viscosity at 100° F. of about 550 seconds Saybolt.

Undoubtedly other types of pumps on the market are satisfactory, and the authors' experience is not particularly comprehensive. The requirement is simply for a pump of reasonably large capacity, capable of maintaining a vacuum of 40 mm. or better. Because leaks usually occur in the system the requirement should preferably be a little more rigid, say a vacuum of 20 mm. in a tight system.

PROCEDURE.

A vacuum distillation is usually made with the cooled residuum from an air distillation, but if a fresh charge of previously "topped" material is to be distilled, 150 c. c. should be weighed or measured into the flask. A new boiling stone is dropped in, as the one used in the air distillation will have become useless during the cooling because of its pores filling with oil.

The three gauze cones are inserted, one at the base of the flask neck, two about a quarter of an inch apart with the rim of the upper cone about an inch below the opening into the side tube. The thermometer is inserted and the flask placed on the electric heater and connected with the condenser. The two cork stoppers holding the thermometer and connecting the flask and condenser are luted with a thick paste of litharge and glycerin (see p. 16). Rubber stoppers and rubber tubing are used for the connections on the cool side of the condenser and ordinarily require no treatment to render them tight. If leaks are suspected, the connections can be coated with the litharge-glycerin paste or, preferably, painted with shellac or a mixture of shellac and lamp black. The latter mixture has a little more body than the plain shellac, and is preferred by the authors.

It was first used in the Bureau of Mines laboratory as an oil-proof marking ink for cans and bottles, but has since been used for many purposes. It is an excellent black varnish and is suitable for closing up leaky joints or stoppers. It does not, of course, stand heat and can not be substituted for the litharge-glycerin paste where the latter is usually employed.

The other parts of the set of apparatus are adjusted and the vacuum pump started. Plate I, *A* (see p. 24), shows the apparatus used in the Pittsburgh petroleum laboratory of the Bureau of Mines. The position of some of the parts, although satisfactory for the purpose of showing in a picture, could be modified to advantage in actual use.

If an automatic control device is used, the oil can be heated immediately. If the vacuum is controlled manually it should be adjusted before heating or at least before the oil has reached its boiling point. After boiling has started the heat is regulated so that distillation proceeds at a rate of from 1 to 2 drops a second. A faster rate may cause violent boiling of the oil and the three gauze cones may fail to catch all the liquid of the spray.

The temperature of the condenser water is maintained at about 60° C. (140 F.). This prevents the solidification and accumulation of paraffin wax in the condenser tube and reduces the viscosity of distillates so that lag between the distilling flask and receiving graduate is minimized.

TABLE 4.—*Results of distillation analyses of samples of typical Pennsylvania and Mid-Continent crude petroleum.*

Item.		Pennsylvania crude (Laboratory No. 00378).					Mid-Continent crude (Laboratory No. 00385).				
		Per cent, fraction.	Sum per cents.[a]	Specific gravity of fraction.	Viscosity of fraction.[b]	Cloud test of fraction, °F.	Per cent, fraction.	Sum per cents.[a]	Specific gravity of fraction.	Viscosity of fraction.[b]	Cloud test of fraction, °F.
Distillation at atmospheric pressure.											
TEMPERATURE LIMITS.											
°C.	*°F.*										
Up to 50	Up to 122	0.9	0.9	0.667			0.2	0.2	0.728		
50- 75	122-167	2.6	3.5		....	....	0.8	1.0		....	....
75-100	167-212	3.8	7.3	.717	....	....	3.3	4.3			
100-125	212-257	7.0	14.3	.744	....	....	3.8	8.1	.749	....	....
125-150	257-302	5.7	20.0	.762	....	....	6.2	14.3	.766	....	....
150-175	302-347	4.9	24.9	.774	....	....	5.5	19.8	.787	....	....
175-200	347-392	4.7	29.6	.786	....	....	5.2	25.0	.804	....	....
200-225	392-437	4.5	34.1	.795	....	....	5.7	30.7	.813	....	....
225-250	437-482	5.8	39.9	.803	....	....	6.7	37.4	.828	....	....
250-275	482-527	7.0	46.9	.816	....	....	8.1	45.5	.845	....	....
Vacuum distillation at 40 mm.											
TEMPERATURE LIMITS.											
°C.	*°F.*										
150-175	302-347	0.3	0.3	.823	....	9	0.3	0.3	.856	....	5
175-200	347-392	4.8	5.1				4.1	4.4			
200-225	392-437	5.8	10.9	.829	....	39	6.4	10.8	.870	38.4	34
225-250	437-482	6.5	17.4	.841	51.3	54	5.7	16.5	.882	60.3	46
250-275	482-527	5.7	23.1	.861	78.1	68	5.4	21.9	.885	113.3	73
275-300	527-572	5.2	28.3	.870	114.5	75	6.2	28.1	.904	196.1	86

[a] Sum per cents are divided at the point between air fractions and vacuum fractions.
[b] Saybolt Universal viscosity, at 100° F.

A fraction is separated, or a reading of the volume distilled is made at the first 25° C. mark above the temperature read when the first drop falls from the end of the condenser tube. With a residuum distilled at atmospheric pressure to 275° C. the first drop in the vacuum distillation generally falls at a temperature between 160 and 170° C. and the first fraction is separated at 175° C. Further fractions are separated (or readings are taken) at each of the subsequent 25° marks, 200° C., 225° C., etc. Distillation can ordinarily be carried safely to a vapor temperature of 300° C., and with some oils to even a higher mark. However, 300° C. is usually regarded as a satisfactory limit. When this temperature is reached the pump is cut off and a valve opened into the system which increases the pressure and stops boiling almost instantaneously. A few minutes are allowed for the condenser tube to drain and the receiving container is opened and the tube removed. The volume collected in each tube is read and recorded, and the tube is put aside if further examination is required.

INTERPRETATION OF RESULTS.

The figures obtained for percentages distilling between given temperatures are of some value in comparing different samples of crude oil but are not sure indicators of commercial value, which generally depends on other properties than volatility. The fractions are therefore usually subjected to further examination, as described on page 37.

Table 4 shows the results of distilling typical samples of Pennsylvania and Mid-Continent crude petroleum at atmospheric pressure and at 40-mm. vacuum.

The specific gravities of the fractions indicate the chemical constitution of the crude oil. Distillates from so-called paraffin-base crudes are of lower specific gravity (higher Baumé gravity) than fractions of the same boiling range from so-called naphthene or asphaltic base oils, or even from "intermediate base" oil such as the Mid-Continent crude represented in Table 4.

The authors have devised a means (see page 45) of measuring the Saybolt viscosities at 100° F. of the various fractions. These viscosity figures indicate the content of the crude oil of lubricating oils of various viscosities. The figures usually can not show the exact results that will be obtained in commercial refining but are, nevertheless, useful for comparisons. For example, Table 3 shows that the fractions from Mid-Continent crude are notably more viscous than fractions of the same boiling range from Pennsylvania crude.

Various methods for testing the content of paraffin wax have been tried, but have not as yet been entirely satisfactory. The "cloud test" (see p. 53) which is used at present gives the temperatures at which paraffin crystals start to form, and although it is more qualitative than quantitative, it indicates whether one crude probably contains more or less paraffin than another.

The properties of the residuum in the flask after completion of the vacuum distillation are important in determining whether or not a given crude will yield a good grade of cylinder stock. One of the important properties of cylinder stock is comparative freedom from asphaltic or pitchy constituents, generally referred to in commercial practice as "tar." The authors have tried several tests for tar and have considered several others. Of the tests tried the Conradson carbon-residue test[7] seemed the most satisfactory. It is given below.

CARBON RESIDUE (CONRADSON METHOD).

The apparatus consists of:

(*a*) Porcelain crucible, wide form, glazed throughout, 25 to 26 c. c. capacity, 46 mm. in diameter.

(*b*) Skidmore iron crucible, 45 c. c. (1.5 oz.) capacity, 65 mm. in diameter, 37 to 39 mm. high with cover, without delivery tubes, and one opening closed.

(*c*) Wrought-iron crucible with cover, about 180 c.c. capacity, 80 mm. diameter, 58 to 60 mm. high. At the bottom of this crucible a layer of sand is placed about 10 mm. deep, or enough to bring the Skidmore crucible with cover on nearly to the top of the wrought-iron crucible.

(*d*) Triangle, pipe stem covered, projection on side so as to allow flame to reach the crucible on all sides.

(*e*) Sheet-iron or asbestos hood provided with a chimney about 2 to 2.5 inches high, 2.125 to 2.25 inches in diameter to distribute the heat evenly during the process.

(*f*) Asbestos or hollow sheet-iron block, 6 to 7 inches square, 1.25 to 1.5 inches high, provided with opening in center 3.25 inches in diameter at the bottom and 3.5 inches in diameter at the top.

The test shall be conducted as follows:

Ten grams of the oil to be tested are weighed in the porcelain crucible, which is placed in the Skidmore crucible and these two crucibles are set in the larger iron crucible, being careful to have the Skidmore crucible set in the center of the iron crucible, covers being applied to the Skidmore and iron crucibles. Place on triangle and suitable stand with asbestos block and cover with sheet iron or asbestos hood in order to distribute the heat uniformly during the process.

Heat from a Bunsen burner or other burner is applied with a high flame surrounding the large crucible until vapors from the oil start to ignite over the crucible, when the heat is slowed down so that the vapor (flame) will come off at a uniform rate. The flame from the ignited vapors should not extend over 2 inches above the sheet-iron hood. After the vapor ceases to come off the heat is increased as at the start and kept so for 5 minutes, making the

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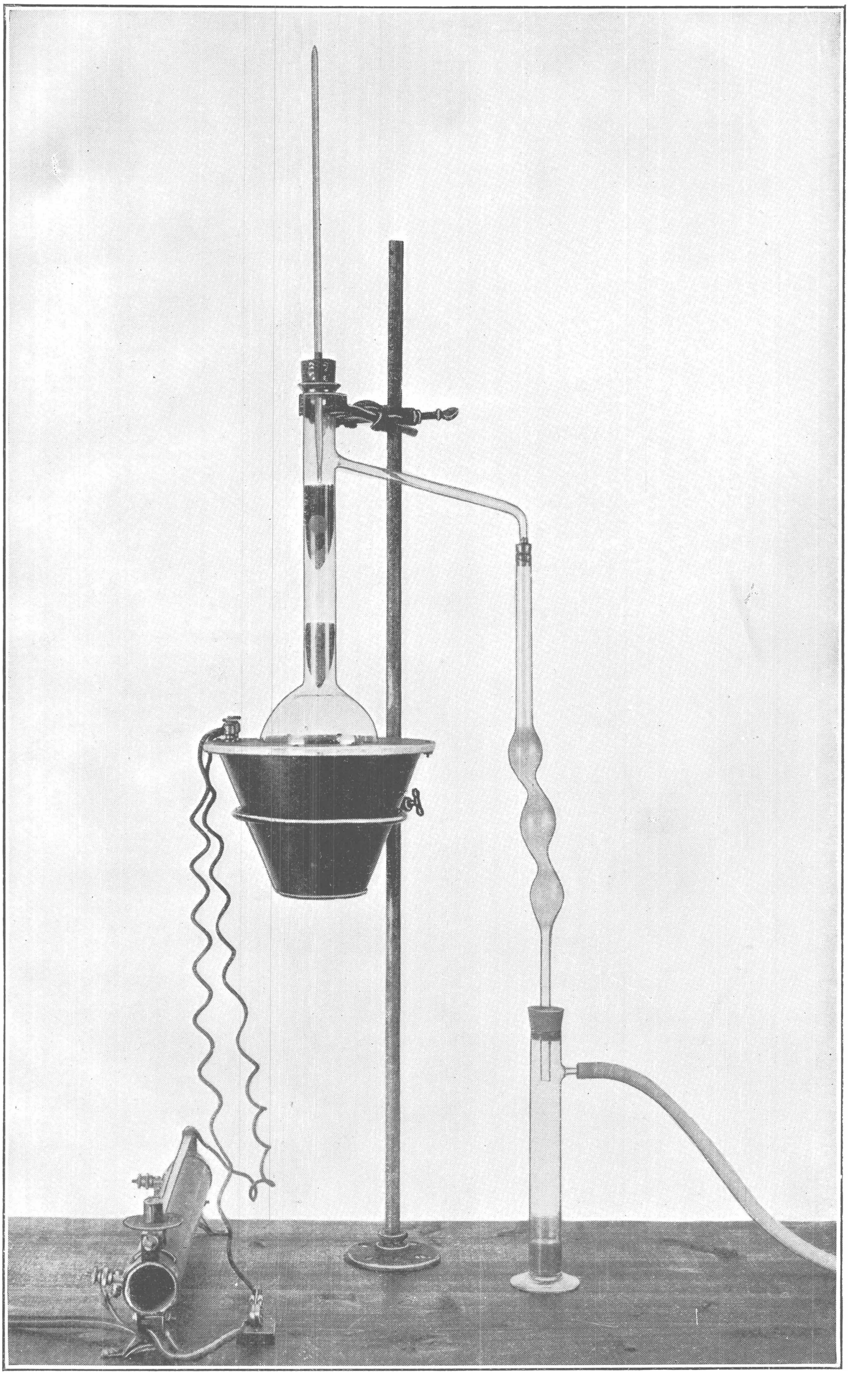
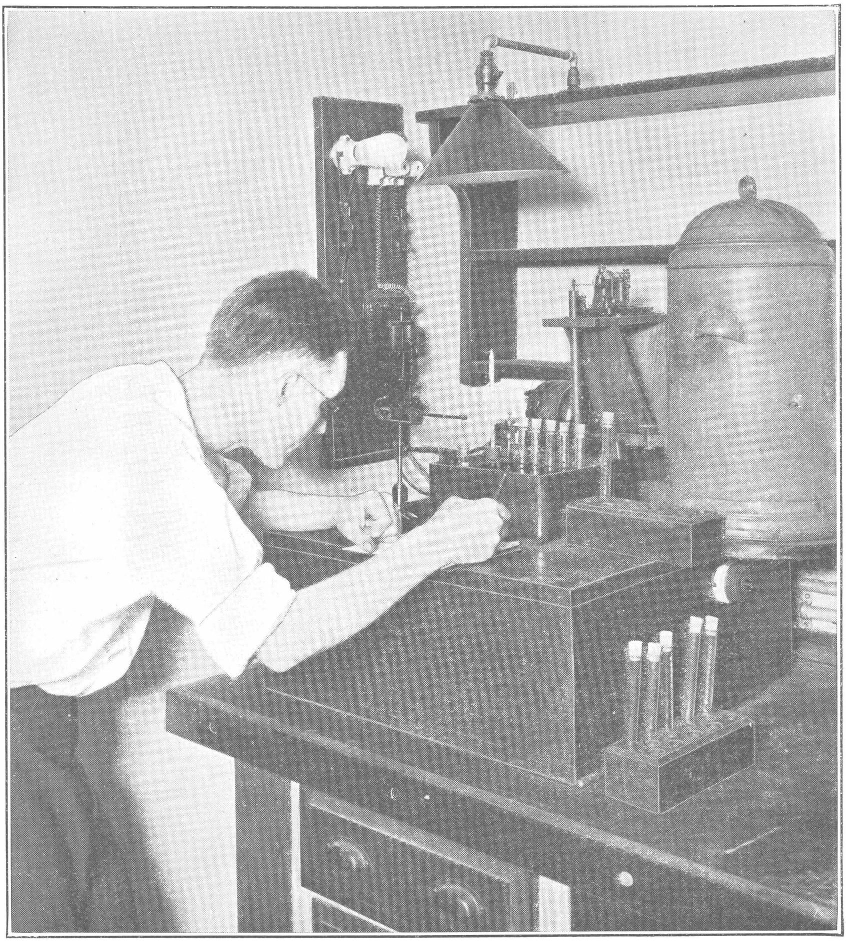
[7] Standard tests for lubricants, Am. Soc. Test. Mats.: A. S. T. M. standards, 1918, pp. 620–622.



ASSEMBLY OF APPARATUS FOR ROUTINE DISTILLATION OF LUBRICATING OIL.



THERMOSTAT BATH FOR MEASURING SPECIFIC GRAVITY AT 60° F.

lower part of the large crucible red hot, after which the apparatus is allowed to cool somewhat before uncovering the crucible. The porcelain crucible is removed, cooled in a desiccator, and weighed.

The entire process should require about one-half hour to complete when heat is properly regulated. The time will depend somewhat upon the kind of oil tested, as a very thin, rather low flash-point oil will not take as long as a heavy, thick, high flash-point oil.

Two minor modifications have been introduced in this test. Because of greater durability a silica instead of a porcelain crucible is used. The quantity of oil is usually 5 grams instead of 10 grams, as the carbon residues from the oils tested by the authors are generally considerably greater than those obtained from refined lubricating oils, for which the test was planned.

The results obtained up to date with this test agree closely with known facts regarding the behavior of various types of crude oil in the usual processes of commercial refining. For example, crude oils from Pennsylvania and West Virginia yield distillation residuums having carbon residues of from 1 to 3 per cent, whereas Mid-Continent crudes show 6 to 10 per cent and California oils 15 per cent and upward. High-grade cylinder stocks are made from Pennsylvania and West Virginia crudes by relatively simple refining processes. Some Mid-Continent crudes can be worked up into cylinder stock by means of special chemical treatment, but the oils obtained in the California fields are usually regarded as altogether unsuitable for the production of this particular lubricant.

ROUTINE DISTILLATION OF LUBRICATING OIL.

APPARATUS.

The vacuum-distillation method for crude oil previously described can also be used to indicate the source and composition of lubricating oil, with the following modifications. The apparatus shown in Plates I, *B* (see p. 24), and II is the same as that recommended for crude-oil distillation, except for the condenser and receiving system. The former need not be water-jacketed, as lubricating oil rarely contains enough paraffin wax to make trouble through solidification in the condenser. The three-bulbed glass tube shown in figure 5 (p. 11) may be used for the condenser. A straight glass tube has also been used and seemed to be capable of producing satisfactory condensation.

In routine distillation of lubricating oil study of the fractions separated is frequently unnecessary. Accordingly, the modified Bruhl receiver can usually be replaced with a 100-c. c. graduate, preferably with a sealed-on side tube to which the vacuum line is connected.

PROCEDURE.

Measure 150 c. c. of oil into the flask, drop in a boiling stone, and insert gauze cones and thermometer. Connect flask, condenser tube, and receiving graduate with the line to the vacuum pump, pressure-control device, and manometer. Lute the cork joints with litharge-glycerin paste, establish a vacuum of 40 mm., and apply heat enough to maintain a rate of distillation of 1 to 2 drops a second.

Read the temperature of the vapor when the first drop falls from the end of the condenser and the temperatures for each subsequent 5 per cent mark (not 5-c. c. mark, as 5 per cent=7.5 c. c.). Continue the distillation until the first 5 per cent mark above 300° C. (572° F.) is reached.

INTERPRETATION OF RESULTS.

The data at present available are insufficient to warrant a detailed discussion of the subject of interpreting the results of distilling lubricating oils in vacuum. Mention may, however, be made of the fact that so-called naphthene-base oils distill at lower temperatures than products of equivalent viscosity derived from paraffin-base crudes. The vacuum-distillation test also distinguishes "straight" distillates from oils made by blending distillate oils and cylinder stock. It may in addition prove to be of some commercial value. The authors think that perhaps through its use a fairly accurate idea of the "blending formulas" used in producing various brands of lubricating oil might be obtained.

TABLE 5.—*Equivalent specific gravities and degrees Baumé according to the Bureau of Standards equation: Degrees Baumé* $=\frac{140}{\text{specific gravity}}-130$.

S. G.	° B.	S. G.	° B.	S. G.	° B.	S. G.	° B.	S. G.	° B.	S. G.	° B.	S. G.	° B.
0.650	85.4	0.700	70.0	0.750	56·7	0.800	45.0	0.850	34.7	0.900	25.6	0.950	17.4
1	85.1	1	69.7	1	56.4	1	44.8	1	34.5	1	25.4	1	17.2
2	84.7	2	69.4	2	56.2	2	44.6	2	34.3	2	25.2	2	17.1
3	84.4	3	69.1	3	55.9	3	44.3	3	34.1	3	25.0	3	16.9
4	84.1	4	68.9	4	55.7	4	44.1	4	33.9	4	24.9	4	16.8
5	83.7	5	68.6	5	55.4	5	43.9	5	33.7	5	24.7	5	16.6
6	83.4	6	68.3	6	55.2	6	43.7	6	33.6	6	24.5	6	16.4
7	83.1	7	68.0	7	54.9	7	43.5	7	33.4	7	24.4	7	16.3
8	82.8	8	67.7	8	54.7	8	43.3	8	33.2	8	24.2	8	16.1
9	82.4	9	67.5	9	54.5	9	43.1	9	33.0	9	24.0	9	16.0
.660	82.1	.710	67.2	.760	54.2	.810	42.8	.860	32.8	.910	23.8	.960	15.8
1	81.8	1	66.9	1	54.0	1	42.6	1	32.6	1	23.7	1	15.7
2	81.5	2	66.6	2	53.7	2	42.4	2	32.4	2	23.5	2	15.5
3	81.2	3	66.4	3	53.5	3	42.2	3	32.2	3	23.3	3	15.4
4	80.8	4	66.1	4	53.2	4	42.0	4	32.0	4	23.2	4	15.2
5	80.5	5	65.8	5	53.0	5	41.8	5	31.9	5	23.0	5	15.1
6	80.2	6	65.5	6	52.8	6	41.6	6	31.7	6	22.8	6	14.9
7	79.9	7	65.3	7	52.5	7	41.4	7	31.5	7	22.7	7	14.8
8	79.6	8	65.0	8	52.3	8	41.1	8	31.3	8	22.5	8	14.6
9	79.3	9	64.7	9	52.1	9	40.9	9	31.1	9	22.3	9	14.5
.670	79.0	.720	64.4	.770	51.8	.820	40.7	.870	30.9	.920	22.2	.970	14.3
1	78.6	1	64.2	1	51.6	1	40.5	1	30.7	1	22.0	1	14.2
2	78.3	2	63.9	2	51.3	2	40.3	2	30.6	2	21.8	2	14.0
3	78.0	3	63.6	3	51.1	3	40.1	3	30.4	3	21.7	3	13.9
4	77.7	4	63.4	4	50.9	4	39.9	4	30.2	4	21.5	4	13.7
5	77.4	5	63.1	5	50.6	5	39.7	5	30.0	5	21.4	5	13.6
6	77.1	6	62.8	6	50.4	6	39.5	6	29.8	6	21.2	6	13.4
7	76.8	7	62.6	7	50.2	7	39.3	7	29.6	7	21.0	7	13.3
8	76.5	8	62.3	8	49.9	8	39.1	8	29.5	8	20.9	8	13.1
9	76.2	9	62.0	9	49.7	9	38.9	9	29.3	9	20.7	9	13.0
.680	75.9	.730	61.8	.780	49.5	.830	38.7	.880	29.1	.930	20.5	.980	12.9
1	75.6	1	61.5	1	49.3	1	38.5	1	28.9	1	20.4	1	12.7
2	75.3	2	61.3	2	49.0	2	38.3	2	28.7	2	20.2	2	12.6
3	75.0	3	61.0	3	48.8	3	38.1	3	28.6	3	20.1	3	12.4
4	74.7	4	60.7	4	48.6	4	37.9	4	28.4	4	19.9	4	12.3
5	74.4	5	60.5	5	48.3	5	37.7	5	28.2	5	19.7	5	12.1
6	74.1	6	60.2	6	48.1	6	37.5	6	28.0	6	19.6	6	12.0
7	73.8	7	60.0	7	47.9	7	37.3	7	27.8	7	19.4	7	11.8
8	73.5	8	59.7	8	47.7	8	37.1	8	27.7	8	19.3	8	11.7
9	73.2	9	59.4	9	47.4	9	36.9	9	27.5	9	19.1	9	11.6
.690	72.9	.740	59.2	.790	47.2	.840	36.7	.890	27.3	.940	18.9	.990	11.4
1	72.6	1	58.9	1	47.0	1	36.5	1	27.1	1	18.8	1	11.3
2	72.3	2	58.7	2	46.8	2	36.3	2	27.0	2	18.6	2	11.1
3	72.0	3	58.4	3	46.5	3	36.1	3	26.8	3	18.5	3	11.0
4	71.7	4	58.2	4	46.3	4	35.9	4	26.6	4	18.3	4	10.8
5	71.4	4	57.9	5	46.1	5	35.7	5	26.4	5	18.1	5	10.7
6	71.1	6	57.7	6	45.9	6	35.5	6	26.3	6	18.0	6	10.6
7	70.9	7	57.4	7	45.7	7	35.3	7	26.1	7	17.8	7	10.4
8	70.6	8	57.2	8	45.4	8	35.1	8	25.9	8	17.7	8	10.3
9	70.3	9	56.9	9	45.2	9	34.9	9	25.7	9	17.5	.999	10.1
												1.000	10.0

METHODS FOR DETERMINING PHYSICAL PROPERTIES OF DISTILLATION FRACTIONS.

SPECIFIC-GRAVITY DETERMINATION.

Specific-gravity determinations are generally made of all distillation fractions. The degree of accuracy required is usually plus or minus one part in a thousand and the figures are reported to three decimal places. These figures can of course be translated easily into terms of the Baumé scale by the use of any of the several convenient sets of tables such as Table 5. The various methods for measuring specific gravity are discussed briefly as follows:

HYDROMETERS.

Hydrometers are rarely or never used by the Bureau of Mines for measuring the gravity of distillation fractions, as the quantities of oil are usually too small, and if proper accessories are available the specific-gravity balance may be used almost as conveniently as the hydrometer.

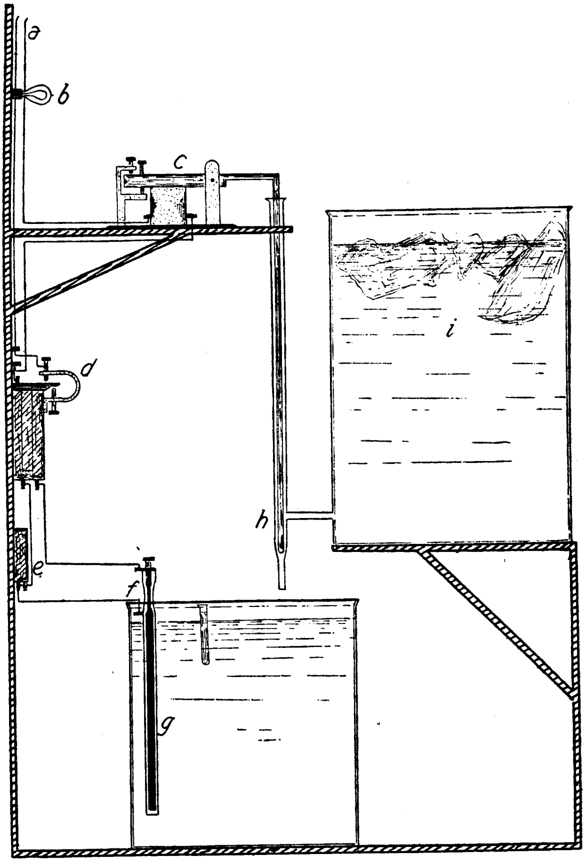


FIGURE 16.—Diagram of temperature-control system for thermostat used for the determination of specific gravity. *a*, 110 or 220 volt d. c. circuit; *b*, lamp in series; *c*, sounder modified to operate valve; *d*, relay; *e*, battery; *f*, regulator; *g*, thermostat; *h*, valve; *i*, reservoir for ice water.

SPECIFIC-GRAVITY BALANCE.

SPECIFIC-GRAVITY THERMOSTAT.

Gravities are practically always reported in the petroleum industry on the basis of the ratio of the densities of oil and water at a temperature of 60° (15.56° C.). A common practice in testing laboratories is to measure gravity at whatever temperature the sample of oil happens to be and correct the results to the standard temperature. Satisfactory correction tables[8] are readily obtainable and are widely used. The bureau prefers to measure gravity at an actual temperature of 60° F. rather than to use the correction tables. Accordingly, a thermostat bath, shown in Plate III (see p. 35), has been installed to maintain this temperature. It consists essentially of a glass battery jar about 13 inches deep and 9½ inches square, surrounded by a wooden case that

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[8] Tagliabue, C. J., Manual for inspectors of petroleum: United States Standard Tables for Petroleum Oils, Bureau of Standards Circular 57, 1916, 65 pp.; Bearse, H. W., and Peffer, E. L., Density and thermal expansion of American petroleum oils: Bureau of Standards Technologic Paper 77, 1916. 26 pp.

serves as a shelf for the instruments and attachments used with the bath. The bath is equipped with a stirrer, mounted in a rack which also serves as a holder for 10 test tubes. An adjustable clamp on one side of the bath is capable of holding in vertical position test tubes of diameters between three-eighths and three-fourths inch. Accessory holders are available for 1¼-inch outside diameter test tubes and for specific-gravity bottles.

A diagram of the temperature-regulating system, which is shown in figure 16, represents a modification of that devised by J. L. R. Morgan.[9] It consists of a thermoregulator operating on a 12-volt direct-current primary circuit and opening or closing a secondary circuit of 110 volts direct current by means of a high resistance telegraphic relay. The latter circuit operates a telegraphic sounder that opens and closes a valve admitting cold water to the jar. When the temperature is higher than 60° F. the primary circuit is closed, this in turn closing the secondary circuit, opening the valve, and admitting cold water until the temperature of the bath is brought down to 60° F. The bath is provided with a constant level overflow outlet, and the stirrer is driven by a small motor that is mounted on the wall back of the bath so as not to cause vibration of the instruments used on the shelf surrounding the glass jar.

A variety of thermoregulators have been tested. The most satisfactory device consists of a copper-sheathed steel tube with a glass top, filled with mercury. A regulator of this type used in one of the bureau laboratories was made in the instrument shop of the Pittsburgh experiment station and has proved highly sensitive and absolutely reliable. It was, however, tedious to make and its construction is not recommended to outside laboratories. A similar regulator, purchased from a chemical supply house, and used in another laboratory of the bureau, was excellent in general design, but certain details of workmanship were poor, and remodeling was necessary before the regulator functioned properly. The most practical regulator for general use in the familiar glass-toluene-mercury type which is easy to make, reliable, and satisfactorily sensitive for all but very small baths. A modification used by the authors (fig. 17) avoids the conventional gooseneck which is rather clumsy and somewhat complicates the process of filling. To fill the tube, invert it with the open end in a beaker of toluene. Part of the air is expelled by cautious warming with a flame, and when a little toluene has been drawn in over the end of the center tube the filling is completed by the customary process of successive boiling and cooling. After both

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[9] Morgan, J. L. R., A simple constant temperature bath for use at temperatures both above and below that of the room: Jour. Am. Chem. Soc., vol. 33, 1911, pp. 344–349.

inner and outer tubes are completely filled, the regulator is righted, placed in a bath at a temperature slightly higher than is to be maintained in actual service, and mercury is run in to displace the toluene in the center tube. This procedure insures enough mercury in the bottom of the regulator so that toluene will not slip past if the regulator becomes moderately overheated in subsequent service.

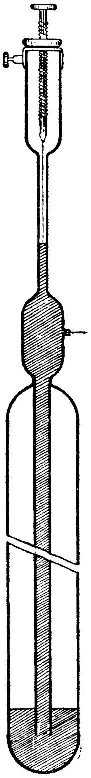

FIGURE 17.—Glass-toluene-mercury thermometer. Glass walls are inked solid, toluene space is white, and mercury space is shown in cross-hatching.

The authors suggest also the possibility of using one of the convenient types of bimetallic thermoregulator at present on the market in place of either the glass-toluene or steel-mercury devices. One type of bimetallic regulator that the authors have used is capable of breaking a current of 100 to 150 watts.

USE OF SPECIFIC-GRAVITY BALANCE.

When quantities of 15 c. c. or more of oil are available a standard Westphal specific gravity balance, with a plummet of about 5 c. c. displacement may be used. The test tube containing the sample of oil should have an internal diameter at least three-sixteenth inch greater than the maximum diameter of the plummet. The accuracy of the balance should be tested by trial with distilled water or other liquid of known density. Before it is used for a series of determinations it should be carefully leveled with the plummet hanging in an empty tube held in the special clamp already mentioned. If the instrument is notably out of balance, adjustment should be made by changing the weight either of the plummet and its attachments or of the pointer end of the beam. It may be finally adjusted by the leveling screw on the base. A good Westphal balance, if properly handled, is rarely out of adjustment and the usual procedure involves making sure that the points on the frame and beam come in line when the balance is set in place. The balance should be set on a carefully leveled plate of glass or metal, as a wooden surface is apt to be slightly uneven.

Actual measurements are made by adjusting weights on the beam of the balance until the two points come in line. For ordinary work no more than three of the four sizes of weights usually provided with the instrument need be used. Only two sizes of weights can be used if final adjustment is secured by moving the smaller weight between notches on the beam and estimating tenths of a division.

For quantities of oil between 5 c. c. and 15 c. c. a Westphal balance with small plummet can be used. A type that has been made abroad, and which is apparently difficult to obtain at present in the United States, has a plummet of about 1 c. c. displacement and is correspondingly smaller in other dimensions than the usual 5-c. c. size. The authors have extensively used a balance of this type, and have also used an American-made "Chainomatic" specific-gravity balance with a plummet of 2 c. c. displacement.

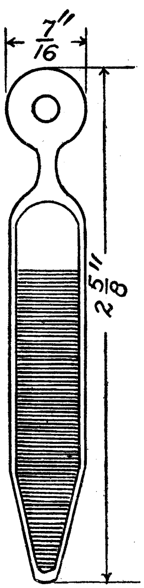

FIGURE 18.—Section of small plummet for Westphal balance.

USE OF LARGE WESTPHAL BALANCE WITH SMALL PLUMMET.

A convenient method for determining the specific gravity of small quantities of liquid is described by Weiss.[10] A small plummet, made of 1 to 2 c. c. displacement (see fig. 18), is attached to a platinum wire and a hook and used on a regular, large-sized Westphal balance, and is calibrated by determining the readings on the Westphal balance beam necessary to balance the plummet in air and distilled water. By determining the weight necessary to balance the plummet in the oil to be tested the specific gravity of the latter can be calculated according to the following relation: Sp. gr. $=\frac{o-a}{w-a}$, where

o=weight necessary to balance plummet in oil,
a=weight necessary to balance plummet in air, and
w=weight necessary to balance plummet in water.

USE OF PICNOMETER.

When the quantity of oil to be tested is less than 5 c. c. some sort of a picnometer must often be used. A convenient type has been devised by Drushel, and is described in Bulletin 125, Bureau of Mines.[11] The form and dimensions are shown in figure 19. The instrument is a capillary pipette with a bulb of capacity between 1 and 2 c. c. The oil is first brought to the desired temperature, then the picnometer is filled to the mark by suction. A bit of rubber tubing is used as a mouthpiece. The rubber tubing is removed, the outside of the picnometer wiped dry, and its weight determined to the nearest milligram. From this weight is sub-

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[10] Weiss, J. M., Specific gravity—its determination for tars, oils, and pitches: Jour. Ind. and Eng. Chem., vol. 7, 1915, pp. 21-24.

[11] Rittman, W. F., and Dean, E. W., The analytical distillation of petroleum: Bull. 125, Bureau of Mines, 1916, p. 27.

tracted the weight of the empty instrument. Specific gravity is calculated by dividing the result thus obtained by the weight of pure water at 60° F. held by the instrument.

The use of the Drushel picnometer depends upon the fact that the capillary tip prevents flow of the oil in either direction, provided it is kept approximately horizontal. The bore of this tip should be made to vary somewhat according as the picnometer is to be used for light, medium, or very viscous oils. When distillates of the gasoline range are to be tested an instrument should be selected that has a long, fine capillary tip. For the other extreme, distillates of the lubricating-oil fraction, the tip should be shorter and of larger bore, otherwise filling the picnometer will be extremely difficult.

MEASUREMENT WHEN PARAFFIN WAX CRYSTALLIZES AT 60° F.

Some of the distillates obtained in the vacuum distillation contain paraffin wax that crystallizes above a temperature of 60° F. These fractions are usually tested for specific gravity at 100° F. (37.8° C.), which is above the crystallizing temperatures ordinarily encountered. Results are corrected to 60° F. by the usual tables. These correction tables are not strictly accurate for oils that contain paraffin wax, as the relation for expansion with varying temperature changes as the solidifying point is approached. The discrepancies thus introduced, however, are regarded as practically negligible.

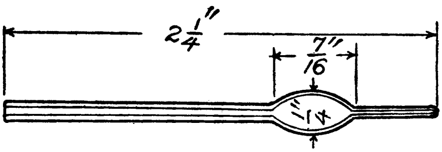

FIGURE 19.—Form and approximate dimensions of Drushel picnometer.

MEASUREMENTS FOR VERY VISCOUS OILS.

None of the methods just described are satisfactory for measuring the specific gravities of very viscous products, such as the residues from vacuum distillations. The following method has been used by the authors.

The measurements are made in ordinary specific-gravity bottles as shown in figure 20. The size selected depends on the quantity of oil available and may be between 5 c. c. and 25 c. c.; the latter is preferred if enough oil is at hand. These bottles are made approximately to size but should be carefully calibrated by the user, by weighing first dry and then filled with distilled water at 60° F.

Actual calibration of the bottle is made as follows:

Fill each bottle with distilled water, place in a water bath maintained within plus or minus 0.2° of 60° F. Keep the bottle in the bath for at least 15 minutes, then insert the stopper and press it down firmly, and be sure that water flows out through the perforation. Remove the bottle from the bath. Immediately wipe the top of the stopper dry, then wipe the rest of the bottle dry. Do not disturb the small drop of water that subsequently collects above the perforation as the temperature of the water in the bottle increases to that of the room. Weigh to the nearest milligram. From the weight obtained subtract *T* (the tare weight of the bottle), and record the resulting figure as *C*, which may be called the capacity of the bottle.

After calibrating bottles according to the method described above the actual determination of specific gravity is carried out as follows:

(*a*) Heat the sample of oil to approximately 50° C. (122° F.) and keep at this temperature for about 10 minutes, so that all air bubbles escape from the oil. Fill the specific-gravity bottle to a point just below the portion of the neck that is occupied by the stopper. If oil is on the surface with which the stopper will come in contact, wipe it out thoroughly with filter paper or lint-free cloth. Insert the stopper and allow the bottle to come approximately to room temperature, as otherwise satisfactory weighing can not be made. Weigh the bottle and oil and record the figure obtained as *Wo*, weight of bottle plus oil.

(*b*) Remove the stopper from the specific-gravity bottle and fill the neck even full with distilled water. Suspend in water bath at 60° F. for at least 15 minutes, then insert the stopper and immediately wipe off the top of the stopper, after which the rest of the bottle can be dried. The procedure is the same as that described in a preceding paragraph, and particular care should be taken not to disturb the drop of water collecting above the perforation, which appears when the contents of the bottle begin to warm up to room temperature. Weigh the bottle and its contents to the nearest milligram and record as *Woa*.

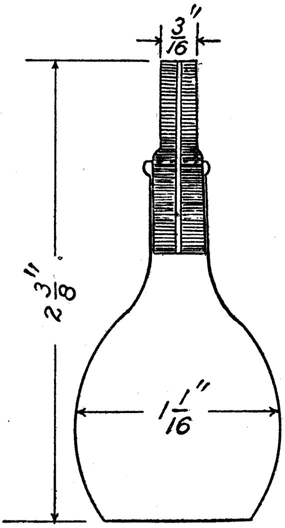

FIGURE 20.—Specific-gravity bottle.

(*c*) The specific gravity is calculated as follows:

T=tare weight of bottle.
C=capacity of bottle.
Wo=weight of bottle plus oil.
Woa=weight of bottle plus oil and water.
O=weight of indeterminate quantity of oil in bottle.

A=weight of indeterminate quantity of water in bottle.
V=volume of indeterminate quantity of oil in bottle.

$$Wo - T = O$$
$$Woa - Wo = A$$
$$C - A = V$$
$$\frac{O}{V} = \text{Sp. gr. at } 60^\circ.$$

This method is a little more tedious than any of those already described, but is, according to the authors' experience, the most convenient means of obtaining reliable gravity determinations with very viscous or pitchy oils.

VISCOSITY.

The quantities of the various fractions obtained in the routine distillation of crude petroleum are never large enough to permit testing in any of the types of viscosimeters commonly used in the petroleum industry. A special instrument is, therefore, needed. The general requirements, in addition to ability to work with small quantities, are simplicity and ruggedness in construction, rapidity in operation, and results that can be expressed in terms familiar to men in the petroleum industry. An accuracy of plus or minus 2 per cent is regarded as adequate.

TEMPERATURES AT WHICH VISCOSITIES SHOULD BE MEASURED.

The general custom in the petroleum industry in the United States is to measure the viscosity of the lighter lubricating oils, which are frequently classed as "neutral" oils, at a temperature of 100° F. Heavy lubricating oils, such as cylinder stocks and valve oils, are tested at 210° F. Certain special products are tested at 130° F., this temperature being recommended for so-called "black oils." For the present work it has seemed adequate to test the viscosity of distillates at 100° F. and of residuums at 212° F. The latter has been chosen instead of 210° F. because of operating convenience and because the difference in viscosity due to a variation of 2° F. at this temperature is less than the ordinary experimental error.

UNITS FOR EXPRESSING RESULTS.

The theoretically desirable units for the expression of viscosity results are without question those of the c. g. s. system. At present, however, these are rarely used by the petroleum industry in the United States and are unfamiliar to the average petroleum technologist; therefore the unit most commonly employed, the Saybolt second, has been used in these experiments.

SELECTION OF AN INSTRUMENT.

Perhaps the most familiar type of instrument for measuring the viscosity of small volumes of liquids is Ostwald's modification of Poiseuille's apparatus.[12] This instrument has been considerably improved by several recent investigators,[13] whose modified devices are more accurate, but also more complex in construction and operation. For the present work simplicity and convenience are needed more than a high degree of accuracy, and the authors have accordingly devised the instrument described below. This so-called "pipette viscosimeter" is simple to construct and operate, is rugged and yields results that are at least as accurate as those obtained with any of the ordinary short-tube viscosimeters of the petroleum industry.

BUREAU OF MINES PIPETTE VISCOSIMETER.

The instrument recommended by the authors is a small capillary pipette with a ground tip. Approximate dimensions that have seemed satisfactory are indicated in figure 21. The instrument is made of a piece of capillary glass tubing of about 1 mm. bore and 6 mm. outside diameter with a bulb blown in it of about 1 to 1.5 c. c. capacity. On one side of the bulb is about 12.5 cm. of capillary with a ground or fire polished end. On the other side of the bulb is 30 mm. of capillary with a tip ground almost but not quite to a point. Circular marks are etched just below and above the bulb and it is usually convenient to etch also in the bulb a designating number or symbol. The accessories used with the pipette and their assembly are described on page 14.

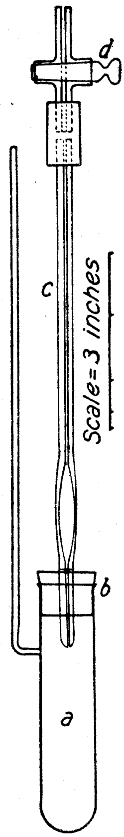

FIGURE 21.—Pipette viscosimeter and accessories. *a*, Receiving test-tube with sealed-on pressure-equalizing tube; *b*, cork or rubber stopper; *c*, pipette viscosimeter; *d*, stopcock attached to upper end of pipette viscosimeter.

CALIBRATION OF PIPETTE VISCOSIMETERS IN TERMS OF SAYBOLT SECONDS.

The most obvious method of calibrating a pipette viscosimeter in terms of "Saybolt seconds" is to determine and then plot graphically the efflux times

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[12] Findlay, Alexander, Practical physical chemistry, 1911, p. 72.

[13] Holde-Mueller, The examination of hydrocarbon oils, 1915, pp. 117–119; Bingham, E. C., The variable pressure method for the measurement of viscosity: Proceedings of the American Society for Testing Materials, vol. 48, part 2, 1918, pp. 374–386; Bingham, E. C., and Jackson, R. F., Standard substances for the calibration of viscosimeters: Bulletin of the Bureau of Standards, vol. 14, 1918, pp. 59–86.

of a series of oils of varying viscosities measured with both instruments. The curve thus obtained can be used to make the desired transformations or a table of equivalents can be prepared from it. This method has been used by the authors and is reasonably satisfactory. The only objection is the large number of points that should be determined in order to obtain a curve that obviates discrepancies due to experimental error. This difficulty is avoided by the use of a method indicated by the following considerations.

The following simple equation[14] expresses the relation between viscosity in c. g. s. units and the instrumental readings obtained with efflux-jet viscosimeters:

$$V_k = At - \frac{B}{t} \tag{1}$$

V_k is the so-called kinematic viscosity, which is absolute viscosity in poises divided by the density of the liquid tested. t is the efflux time, usually expressed in seconds. A and B are instrumental constants.

If the rate of flow of the liquid through the efflux tube is slow enough, the term $\frac{B}{t}$ becomes negligible in comparison with the term At and the equation can be used in the linear form:

$$V_k = At \tag{2}$$

That is, kinematic viscosity may be regarded as directly proportional to efflux time.

Herschel[15] has derived values of the constants A and B for a Saybolt universal viscosimeter of normal dimensions which appear in the following equation:

$$V_k = 0.00220\ t_s - \frac{1.80}{t_s} \tag{3}$$

A series of calculations has indicated that when the value of t_s, the efflux time for the Saybolt instrument, or so-called Saybolt viscosity, approaches 300 seconds, the second term of the equation is approximately 1 per cent of the first and for present needs in the line of accuracy may be disregarded. It follows, therefore, that when t_s, the Saybolt viscosity, is 300 seconds or more, equation (3) may be used in the following simplified form:

$$V_k = 0.00220\ t_s \tag{3a}$$

The general dimensions of the pipette viscosimeter are such that, for oils of equal viscosity, pipette efflux times and Saybolt efflux

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[14] Herschel, W. H., Standardization of the Saybolt universal viscosimeter: Bureau of Standards Technologic Paper 112, 1919, p. 9.

[15] Work cited, p. 19.

times are about the same. The quantity of liquid flowing from the Saybolt instrument is 60 c. c. and that from the pipette viscosimeter about 1.5 c. c. The rate of flow is considerably less with the pipette than with the Saybolt viscosimeter, and therefore the linear relationship between kinematic viscosity and efflux time obviously exists for smaller values of the latter with the pipette than with the Saybolt tube. No attempt has been made to determine the limiting pipette efflux time corresponding to the figure of 300 seconds calculated for the Saybolt, but it is without question lower than 40 seconds. For all practical purposes, therefore, the relationship between kinematic viscosity and pipette efflux time may be expressed by the equation

$$V_k = A_p t_p \tag{4}$$

in which A_p is an instrumental constant characteristic of each pipette viscosimeter.

TABLE 6.—*Kinematic viscosities* (V_k) *equivalent to Saybolt viscosities* (t_s) *according to Bureau of Standards equation*

$$V_k = 0.00220 t_s - \frac{1.80}{t_s}$$

t_s	v_k	t_s	v_k	t_s	v_k	t_s	v_k	t_s	v_k	t_s	v_k	t_s	v_k
		50	0.0740	100	0.2020	150	0.3180	200	0.4310	250	0.5428		
		1	.0769	1	.2044	1	.3203	1	.4332	1	.5450		
		2	.0798	2	.2068	2	.3226	2	.4355	2	.5473		
		3	.0826	3	.2091	3	.3248	3	.4377	3	.5495		
		4	.0855	4	.2115	4	.3271	4	.4400	4	.5517		
		5	.0883	5	.2139	5	.3294	5	.4422	5	.5539		
		6	.0911	6	.2162	6	.3317	6	.4445	6	.5562		
		7	.0938	7	.2186	7	.3339	7	.4467	7	.5584		
		8	.0966	8	.2209	8	.3362	8	.4490	8	.5606		
		9	.0993	9	.2233	9	.3385	9	.4512	9	.5629		
		60	.1020	110	.2256	160	.3408	210	.4534	260	.5651		
		1	.1047	1	.2280	1	.3430	1	.4557	1	.5673		
		2	.1074	2	.2303	2	.3453	2	.4579	2	.5695		
		3	.1100	3	.2327	3	.3476	3	.4602	3	.5718		
		4	.1127	4	.2350	4	.3498	4	.4624	4	.5740		
		5	.1153	5	.2374	5	.3521	5	.4646	5	.5762		
		6	.1179	6	.2397	6	.3544	6	.4669	6	.5784		
		7	.1205	7	.2420	7	.3566	7	.4691	7	.5807		
		8	.1231	8	.2444	8	.3589	8	.4713	8	.5829		
		9	.1257	9	.2467	9	.3612	9	.4736	9	.5851		
		70	.1283	120	.2490	170	.3634	220	.4758	270	.5873		
		1	.1309	1	.2513	1	.3657	1	.4781	1	.5896		
		2	.1334	2	.2537	2	.3679	2	.4803	2	.5918		
		3	.1359	3	.2560	3	.3702	3	.4825	3	.5940		
		4	.1385	4	.2583	4	.3725	4	.4848	4	.5962		
		5	.1410	5	.2606	5	.3747	5	.4870	5	.5985		
		6	.1435	6	.2629	6	.3770	6	.4892	6	.6007		
		7	.1460	7	.2652	7	.3792	7	.4915	7	.6029		
		8	.1485	8	.2675	8	.3815	8	.4937	8	.6051		
		9	.1510	9	.2699	9	.3837	9	.4959	9	.6074		
		80	.1535	130	.2722	180	.3860	230	.4982	280	.6096		
		1	.1560	1	.2745	1	.3883	1	.5004	1	.6118		
32	0.0142	2	.1585	2	.2768	2	.3905	2	.5026	2	.6140		
3	.0181	3	.1609	3	.2791	3	.3928	3	.5049	3	.6162		
4	.0219	4	.1634	4	.2814	4	.3950	4	.5071	4	.6185		
5	.0256	5	.1658	5	.2837	5	.3973	5	.5093	5	.6207		
6	.0292	6	.1683	6	.2860	6	.3995	6	.5116	6	.6229		
7	.0328	7	.1707	7	.2883	7	.4018	7	.5138	7	.6251		
8	.0362	8	.1732	8	.2906	8	.4040	8	.5160	8	.6274		
9	.0397	9	.1756	9	.2929	9	.4063	9	.5183	9	.6296		
40	.0430	90	.1780	140	.2951	190	.4085	240	.5205	290	.6318		
1	.0463	1	.1804	1	.2974	1	.4108	1	.5227	1	.6340		
2	.0495	2	.1828	2	.2997	2	.4130	2	.5250	2	.6362		
3	.0527	3	.1853	3	.3020	3	.4153	3	.5272	3	.6385		
4	.0559	4	.1877	4	.3043	4	.4175	4	.5294	4	.6407		
5	.0590	5	.1901	5	.3066	5	.4198	5	.5317	5	.6429		
6	.0621	6	.1925	6	.3089	6	.4220	6	.5339	6	.6451		
7	.0651	7	.1948	7	.3112	7	.4243	7	.5361	7	.6473		
8	.0681	8	.1972	8	.3134	8	.4265	8	.5383	8	.6496		
9	.0711	9	.1996	9	.3157	9	.4288	9	.5406	99	.6518		
										300	.6540		

The relation between pipette efflux time and Saybolt efflux time can obviously be expressed in terms of the following equation:

$$A_p t_p = 0.00220 t_s - \frac{1.80}{t_s} \qquad (5)$$

which is obtained by combining equations (3) and (4). By determining the value of the constant A_p, a curve can be defined corresponding to that obtained by plotting against each other the necessary number of experimentally determined values of t_p and t_s.

DETERMINATION OF THE CONSTANT A_p.

The authors have determined values of the constant A_p as follows: Pipette efflux times are determined for several oils (generally three) of known Saybolt viscosity. Kinematic viscosity figures equivalent to the Saybolt values can be calculated by the use of equation (3) or more conveniently can be taken from Table 6. Figures for the constant A_p can be calculated by using equation (4), and an average of the several values thus obtained is regarded as a reasonably accurate calibration factor for the pipette. This constant may be used to calculate enough equivalent pipette and Saybolt efflux times to plot a satisfactory curve, which is later used. The following simple method of calculation may be used instead of a curve:

PROCEDURE FOR CALIBRATION.

Obtain several oils having Saybolt viscosities covering the approximate range from 40 to 300 seconds at the temperature to be used in tests. The authors regard three as sufficient.

Determine accurately at this selected temperature the Saybolt viscosity of each oil.

Determine accurately at the selected temperature the pipette efflux time of each oil.

From the Saybolt figures use equation (3) or, more conveniently, Table 6 to calculate the kinematic viscosity of each oil.

Divide the kinematic viscosity of each oil by the corresponding pipette efflux time to obtain values of the constant A_p. The several values should be approximately equal, but will normally vary several per cent between extremes. Average these values and take the result as the instrumental constant (A_p) of the pipette.

TABLE 7.—*Calibration of a pipette viscosimeter.*

Type of oil.	Temp. °F.	t_s (Saybolt efflux time).	V_k (from Table 4).	t_p (pipette efflux time).	$A_p=\frac{V_k}{t_p}$
Transformer	100	72	0.1334	61.6	.00217
Spindle	100	189	0.4063	185.3	.00219
Medium auto	100	299	0.6518	299.0	.00218
Average					.00218

$$A_p t_p = 0.00220 t_s - \frac{1.80}{t_s} = V_k$$

$$\frac{A_p}{A_s} = \frac{.00218}{.00220} = 0.99$$

This factor to be used only for viscosities greater than the equivalent of 300 seconds Saybolt.

CALCULATION OF RESULTS BY THE GRAPHIC METHOD.

Prepare a curve on properly selected cross-section paper, calculating the necessary number of points by the use of equation (5), in which the determined value of A_p can now be substituted. A set of typical calibration figures and the resulting equation is shown in Table 6. The curve obtained from these data appears in figure 22. By the use of this curve the Saybolt equivalent up to 300 seconds of any efflux time determined with the pipette can be obtained directly. For pipette efflux times above the range of the graph multiply the experimentally determined figure by a factor obtained by diverting the constant A_p by 0.00220. This factor is in general terms $\frac{A_p}{A_s}$. If the curve had not been calculated many more points would have to be determined experimentally.

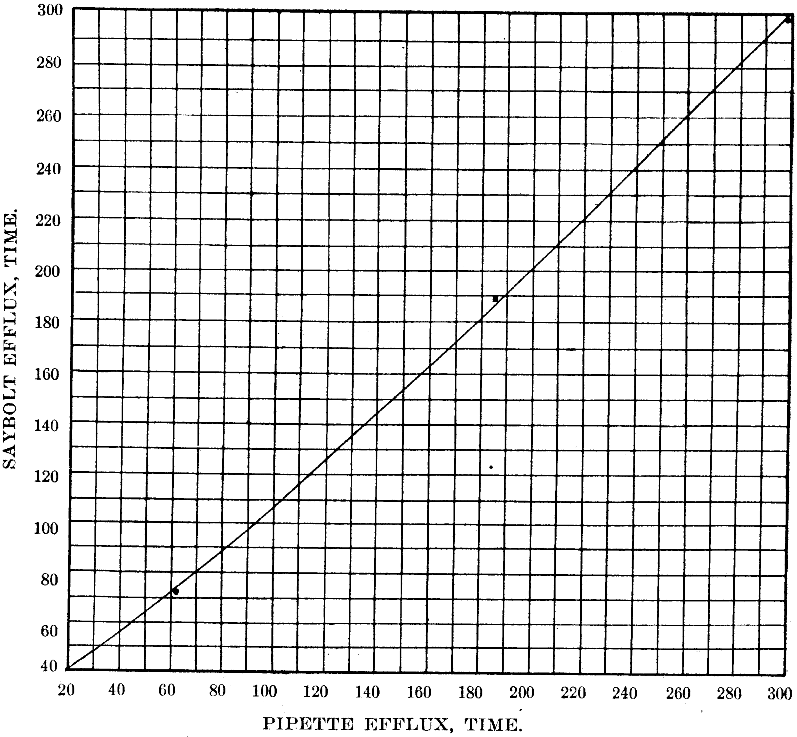

FIGURE 22.—Curve for changing pipette efflux-time into Saybolt equivalents.

CALCULATION OF RESULTS BY THE ARITHMETICAL METHOD.

Multiply the pipette efflux time of the "unknown" oil by the value of A_p. This gives the equivalent kinematic viscosity, V_k.

If V_k is less than 0.6540 (the equivalent of 300 seconds Saybolt) find the Saybolt equivalent in Table 6. The nearest full second is usually satisfactory, but if desired fractions of a second may be determined by interpolation.

If V_k is in excess of 0.6540 divide by 0.00220 or multiply by 454.4, the reciprocal of 0.6540. If preferred the pipette efflux time can, of course, be multiplied directly by the factor $\frac{A_p}{A_s}$, mentioned in the section describing the graphic method. This will ordinarily be preferred as the operator can determine once and for all the pipette efflux time equivalent to 300 seconds Saybolt, and for values in excess of this avoid a trial calculation to determine whether or not the kinematic viscosity is greater than 0.6540.

USE OF THE PIPETTE VISCOSIMETER.

The apparatus required in addition to the viscosimeter is as follows:

A glass stopcock, which is connected with the pipette by means of a piece of heavy-walled rubber tubing or a one-holed rubber stopper. A spring pinchcock, operating on a piece of thin-walled rubber tubing can be substituted.

A small test tube with a sealed-on side tube as indicated in figure 21, or a plain test tube and a properly bent piece of glass tubing that can be inserted through a second hole in the stopper that holds the pipette viscosimeter.

A cork or rubber stopper of proper size and properly bored.

A constant temperature bath of any convenient type having glass walls or a glass window on one side. Temperature regulation should be within plus or minus two or three tenths of a degree Fahrenheit. For tests at 100° F. the authors have used a small thermostat that is obtainable as a stock article from chemical supply houses. For tests at 212° F. use has been made of a convenient type of steam bath, a diagram of which is shown in figure 23. This consists of a copper flask, *b*, heated by gas or an electric hot plate, *a*, a special glass tube which holds the pipette, *e*, and its accessories, a condenser and the necessary glass and rubber connecting tubes similar to those shown in figure 21. Steam is generated in the flask, passes through the glass jacket, *d*, surrounding the viscosimeter, is liquefied in the condenser, *g*, and carried back into the flask by the rubber tube, *h*, to be vaporized again. A side blow-off tube, *c*, is sealed on at the base of the steam jacket tube and can be opened when a viscosimeter is being removed or inserted, thus avoiding danger of being burned. A stopcock, *f*, between the steam jacket and the condenser can be partly closed, thereby building up a little pressure and permitting some regulation of the temperature of the steam. The reflux condenser keeps the copper flask from boiling dry when the set is in use long.

The procedure is as follows: Connect the pipette viscosimeter and glass stopcock and draw in some of the oil to be tested. The bulb of the pipette should be completely filled, also the capillary to a point somewhat above the upper mark. As the pipette must be absolutely clean, it should be washed thoroughly with gasoline after each determination, and the gasoline should be dried out by passing a current of air through the tube. The current of air should preferably be provided by a suction rather than a blast line, though the latter is permissible if a filter such as a loose wad of absorbent cotton is in the line between the air supply and the pipette. When the oil is drawn into the pipette, care should be taken that no saliva enters through the stopcock if suction is applied by mouth. In the Bureau of Mines laboratory the oil is drawn in by means of a rubber bulb of the same type as that used on the pipette which withdraws excess oil from a Saybolt universal viscosimeter.

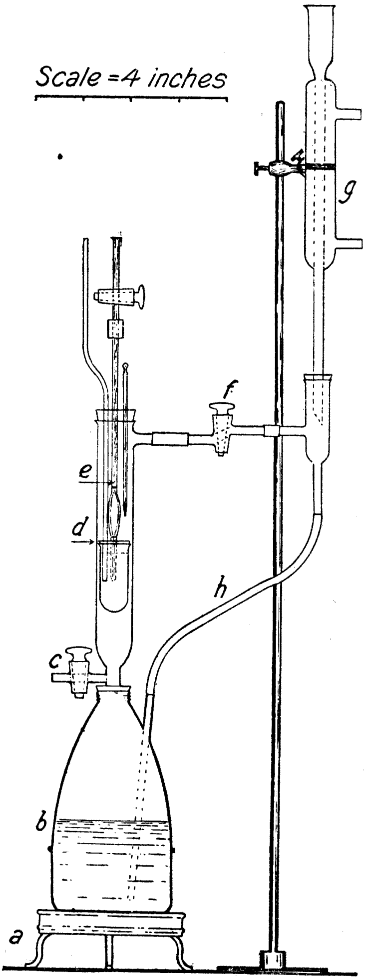

FIGURE 23.—Pipette viscosimeter used with a steam bath: *a*, Electric hot plate; *b*, copper flask; *c*, side blow-off tube; *d*, glass jacket; *e*, pipette; *f*, stopcock; *g*, adapter with condenser above; *h*, rubber tube connecting adapter and flask.

The pipette is filled and inserted in the hole in the stopper of the test tube. If a plain test tube is used instead of the special type shown in figure 23, the pressure-equalizing tube is placed in a second hole in the stopper. The assembled apparatus is placed in the constant temperature bath. The upper level of the charge of oil must be well into the constant temperature zone. The pipette and its contents are allowed to come to the temperature of the bath. Five minutes is usually regarded as time enough, though ten minutes is probably safer. The stopcock above the pipette is opened and when the level of the oil reaches the upper graduation mark a stop watch is started. The watch is stopped when the level of the oil reaches the lower graduation, and the elapsed time is recorded.

An instrument of the pipette type is subject to error, as some of the oil adheres to the walls of the bulb of the pipette. The exact amount of this error has not been determined, but it is probably offset by the fact that it occurs both in calibration and in actual use. The authors have been able to get check results that agree very closely, which indicates that the so-called drainage error is practically constant for oils of like viscosity.

The Saybolt viscosity equivalent to this figure is obtained by either of the methods of procedure previously outlined.

CLOUD TEST.

The cloud test for lubricating oils, as recommended by the American Society for Testing Materials,[16] is not directly applicable to the small quantities of distillates obtained in the bureau method for the routine testing of crude oil samples. In addition, commercial lubricating oils contain relatively small quantities of paraffin and rarely show definite crystallization. The test herein described is actually a crystallizing or solubility test rather than a cloud test in the sense of the definition accepted by the American Society for Testing Materials.

The object of the present test is simply to learn the relative paraffin content of the various fractions as indicated by the temperature at which crystals of wax appear. The results obtained are of value only as a basis of comparison, but although they do not permit direct quantitative interpretation they serve tolerably well to indicate whether the oil tested contains more or less paraffin wax than some oil for which the commercial yields are well known.

PROCEDURE.

Place the set of graduated test tubes containing fractions from the vacuum distillation in a cooling bath containing water at a temperature high enough to keep all the fractions fluid. A temperature of 40° C. (104° F.) will probably be adequate for extreme fractions and 30° C. (86° F.) for ordinary fractions. Place a thermometer, preferably the standard "cloud and pour test" thermometer listed by chemical supply houses, in the tube containing the highest boiling fraction, and be sure that the bulb is properly immersed in the liquid. Add cracked or shaved ice to the water bath and stir vigorously. Remove the tube containing the thermometer occasionally, stir, and

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[16] A. S. T. M. standards, 1918, pp. 617-620.

examine for crystals of paraffin. When these are observed note and record the temperature. Remove the thermometer, wipe clean, and place in the next highest boiling fraction, or, as a matter of precaution, leave the one that has just been tested in the bath and make sure that an abundance of paraffin crystals forms on further cooling. Continue to cool and stir the bath and take further readings. This method of cooling will bring the temperature of the tubes of oil down at a satisfactory rate to approximately 10° C. (50° F.). The fractions needing further cooling down to about 0° C. (32° F.) can be placed in a beaker containing a mixture of cracked or shaved ice and water. For fractions not crystallizing at or above freezing, use first a dry mixture of ice and ordinary salt, NaCl; then, if necessary, an ice brine mixture. This cooling medium works well down to —10° C. (+14° F.) and can, if desired, be made to cool the oil fractions down to —15° C. (+5° F.). Lower temperatures can be attained by the use of other cooling media if desired, but ordinarily all fractions not crystallizing above —15° C. (+5° F.) can be safely reported as "no paraffin crystals at —15° C. (+5° F.)."

SPECIAL DISTILLATION APPARATUS AND METHODS.

The apparatus and methods described on previous pages are adapted primarily to the routine analysis of crude petroleum. The same apparatus is, with slight modification, usable for special types of tests, such as the routine distillation of lubricating oils which has been discussed. Often, however, special apparatus is necessary or desirable. The bureau has developed several special types of stills and accessories, brief descriptions of which are given. Discussion deals principally with the method of construction, as details of operation are subject to so much variation that they could not be treated adequately in this report.

FIVE-GALLON STILL.

Occasionally a still capable of handling an initial charge of 5 gallons of oil has been needed. An installation that has proved satisfactory is shown in figure 24.

BODY OF THE STILL.

The body of this still has an internal diameter of about 13½ inches and an internal height of about 13½ inches. The one made for the authors was bent from a sheet of iron plate three-sixteenths-inch thick, but a piece of well casing or thin-walled iron pipe of approximately the same diameter would have been preferable. A bottom of one-fourth-inch plate was welded in. At the top a flange about 1$\frac{3}{16}$

inches wide, of seven-sixteenths-inch iron plate, was welded on. The flange was drilled with 12 three-eighths-inch holes equally spaced.

The lid of the still was made from a 16-inch circular plate of one-fourth-inch iron. A threaded hole in the center with a reinforcing plate riveted on the under side held the dome or fractionating column, which is described later. The lid was equipped with a thermometer well, consisting of 12 inches of nominal one-fourth-inch iron pipe, the bottom of which was welded closed. The well was screwed to the lid through a hole of proper size. Threads were cut with ordinary tapered tap and die. The lid also held the steam coil, which consisted of approximately 60 inches of nominally one-fourth-inch iron pipe bent in the form of a spiral with two full turns. Thirty-five holes one-sixteenth inch in diameter were drilled in the inner turn of the spiral about three-eighths inch apart and on the under side of the coil. No holes were drilled in the outer turn, the purpose of which is to bring the steam approximately to the temperature of the oil before it is blown through.

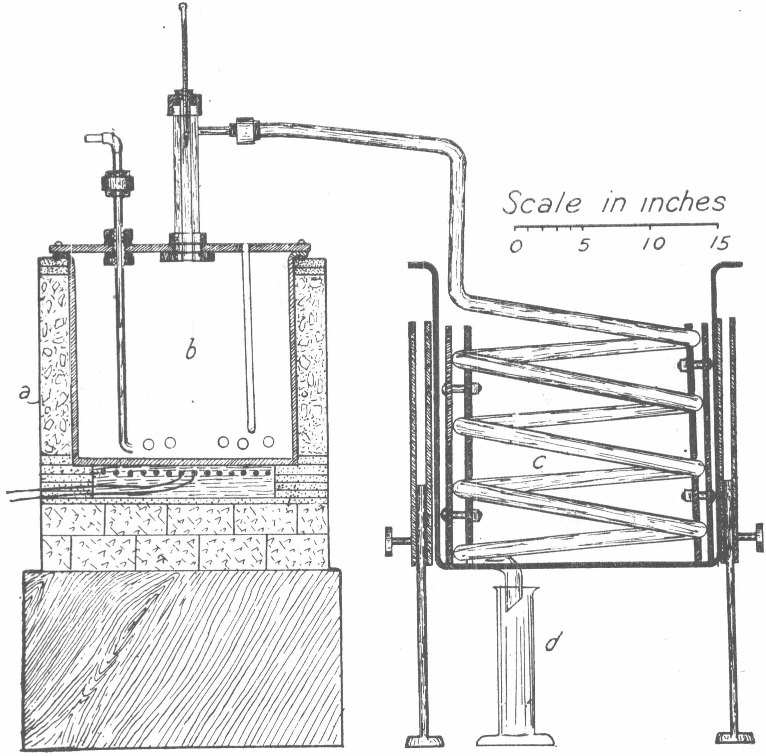

FIGURE 24.—Diagram of still and accessories used for distilling a 5-gallon charge of oil. *a*, Electric heater with insulating jacket surrounding still; *b*, still with fractionating column, steam coil, and thermometer well; *c*, condenser with spiral vapor-tube and surrounding tank of sheet metal; *d*, receiving cylinder.

STILL HEATS.

The still used by the authors is provided with three fractionating columns of varying length according to the purpose to be accomplished. Each of the columns is of nominally 2-inch standard iron pipe with 1 inch of straight-cut threads at the bottom, the respective lengths over all being 7 inches, 9 inches, and 19 inches. Just above the thread is a welded-on ring turned smooth on the under side so as to seat on a gasket, bearing on the lid of the still. Two inches from the top of each column is a welded-in side connection of nominal one-quarter-inch iron pipe sloping downward at an angle of about 75 degrees. The inside of the top of each column is cut with straight threads and holds a brass plug that carries the thermometer. The plug seats on a gasket bearing on the top of the pipe comprising the column.

CONDENSER.

The condenser was made of approximately 15 feet of nominal one-half-inch iron pipe with joints and connections as indicated in figure 24. The coil was mounted in a galvanized-iron tank set on pipe legs with attachments, so that the height of the condenser above the floor can be varied as desired.

ELECTRIC HEATER.

The still is equipped with an electric heater, whose general design appears in figure 24. The heating element is made of two helical coils of nickel-chromium wire embedded in alundum cement. Each of the coils is made by winding 40 feet of No. 12 (B. and S. gage) wire on a one-fourth inch mandrel and stretching to a suitable length. The heating element is made by laying these coils in parallel in spiral form on a well-greased board; the coils are held in position by brads inserted from the under side of the board. A circular ring of thin metal 1¼ inches wide and soldered for the junction is placed on the board and is held in place by brads projecting from the under side. A thick paste of alundum cement is worked in well between the turns of the two coils and the mass is brought level with the edge of the ring, and air-dried for several days. The brads are then drawn, the ring of metal removed by unsoldering with a hot iron, and the heating element is first dried for a day at a temperature of 120–150° C., then fired for half an hour at a good red heat, and mounted in the supporting and insulating case. The latter consists essentially of a transite base and two concentric sheet metal cylinders, riveted or crimped, but not soldered, one about one-half inch larger in diameter than the body of the still, the other about 4 inches larger in diameter

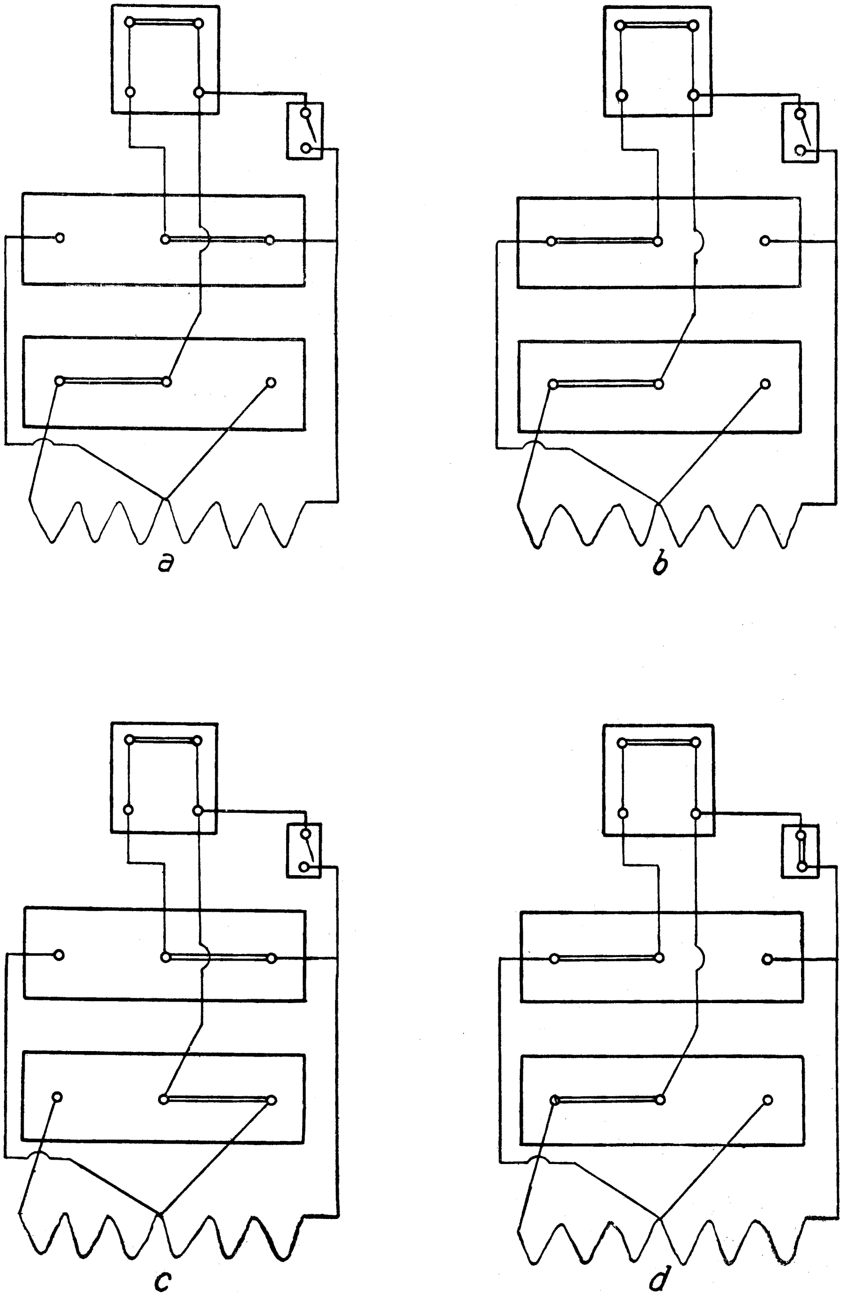

FIGURE 25.—Diagram of electrical connections for heaters built with two parallel resistance coils. *a*, Coils 1 and 2 in series; *b*, coil 1 in circuit; *c*, coil 2 in circuit; *d*, coils 1 and 2 in parallel.

and 2½ inches higher than the first. The insulating material consists of cut or crushed kieselguhr bricks, which fill the spaces between the concentric metal cylinders and are laid in a 2½-inch layer under the heating element. A gasketlike piece of transite, which serves as a cover for the insulating material, is placed at the top between the two sheet-metal cylinders. The two heating coils are connected with a set of switches so arranged that they can be thrown in series or parallel, or used singly as shown in figure 25. A rheostat of 26 ohms resistance and 35 amperes capacity is connected in series with the heating elements and holds the current between 4 amperes and 30 amperes. The rheostat used by the authors is of special construction and not easy to obtain. A water rheostat would probably give satisfactory service or several stock rheostats could be used in series or parallel for the desired range of control.

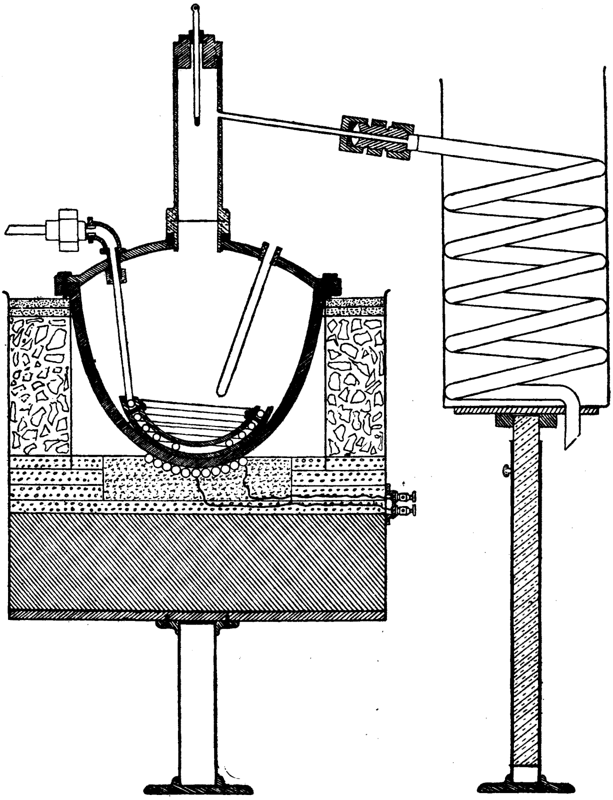

FIGURE 26.—Section of a still designed to handle a charge of 1 gallon of oil.

The selection of a still head depends on the needs of any given distillation. The short dome without fractionating material may be used when only a rough separation of fractions is required. The next longer column with aluminum beads or iron chain for filling material is most generally useful for both air and steam distillation of ordinary crude oils. The longest column is used for close fractionation of low boiling mixtures, such as gasoline or naphtha.

The condenser may be cooled with running water, using an overflow connection, or cracked ice may be kept in the bath. For distillation of lubricating-oil fractions let the condenser water warm up to about 50–60° C. to avoid danger of wax solidifying in the pipe.

For ordinary crude-oil distillation run an air distillation until a vapor temperature of 250 or 275° C. (482 or 527° F.) is reached, then turn in enough steam to maintain the desired rate of distillation. Separation of fractions on the basis of temperature is impractical when steam is used. Cuts can be made either on a basis of percentage or of gravity.

Some details of this still can undoubtedly be modified to advantage. The authors have not made an exhaustive study of its design, nor has it been used as extensively as most of the other apparatus described. It is offered simply as an example of an installation now in use that has given satisfactory results.

ONE-GALLON STILL.

The authors have recently had constructed a still capable of handling a charge of 1 gallon of oil. The essential details of this still are shown in figure 26 and are similar to those of the 5-gallon still just described. The body of the still, however, is a remodeled 2-gallon iron mercury retort. The condenser coil is made of copper tubing, three-fourths inch outside dimension. The still is supplied with fractionating columns of several different lengths. One is about 3 inches from the lid of the still to the outlet tube; the others are approximately 6 and 10 inches.

This still has not been tried out under a range of conditions wide enough to indicate its merit or lack of merit, but it is believed to be of a size and type that will prove decidedly useful in the average petroleum laboratory.

ONE-LITER STILL.

An apparatus for handling a charge of 1 liter of oil has been developed by the bureau and has proved very satisfactory. It can be used with several modifications.

BODY OF STILL.

A good flask for the distillation of noncorrosive liquids such as oil is a 2-liter copper Kjeldahl flask. The neck of the flask should be threaded on the outside to permit attaching a still head unless they are joined with a cork stopper. The general form, dimensions, and type of construction of the still are shown in figures 27 and 28. The brazed-in tube shown in the body of the flask is not part of the stock article but is a convenient accessory. This tube is of copper, of about five-sixteenths-inch internal and thirteen thirty-secondths-inch external diameters and is brazed or silver soldered into the flask. It is used for either filling or partly emptying the flask without disturbing the connections holding the still head, also

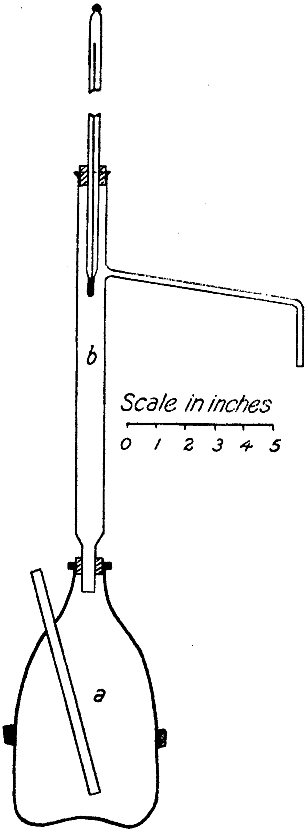

FIGURE 27.—Assembly of a glass still-head with cork connection for distilling a charge of 1 liter of oil. *a,* Copper Kjeldahl flask, nominal 2-liter size, with a brazed-in tube; *b,* glass still-head connected with flask by means of a cork stopper, luted with litharge-glycerin paste. Fractionating column has filling material (not shown), such as iron chain or aluminum beads.

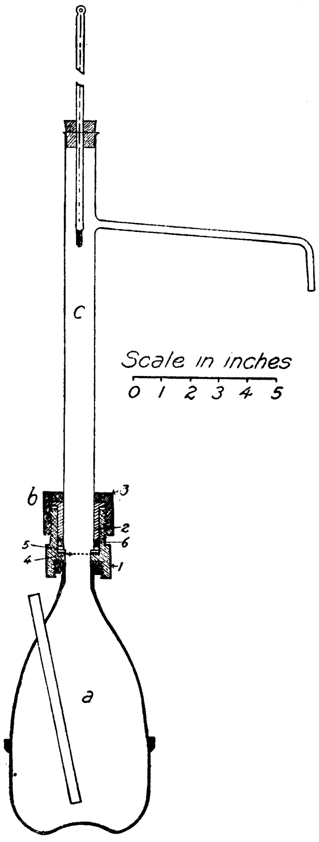

FIGURE 28.—Assembly of a glass still-head with metal union for distilling a charge of 1 liter of oil. *a,* Copper Kjeldahl flask (same as in fig. 27); *b,* metal stuffing-box union consisting of (1) body connecting with flask and seating on fiber gasket, (2) gland compressing the packing material, which is generally soft asbestos cord saturated with a mixture of graphite and cylinder oil, (3) compression nut, (4) gauze screen that supports the filling material in the fractionating column, (5) two fiber gaskets, the lower serving as a cushion on which the glass tube rests and the upper serving to center the glass tube while the packing is worked in, (6) packing material; *c,* fractionating column of glass with filling material (not shown), such as iron chain or aluminum beads.

for inserting a thermometer or preferably a thermocouple for measuring the temperature of the liquid oil.

A thermocouple for this purpose is made from a suitable length of silk or cotton covered constantin wire, coated 12 to 15 inches with bakelite varnish, over which is drawn 12 to 15 inches of thin-walled copper tubing of internal diameter just large enough to fit the insulated constantin wire snugly. The end where the constantin wire projects through the copper tube is silver soldered to prevent the leakage of any liquid into the interior of the tube. Copper wires of suitable length are soldered to the constantin wire if the cold junction is to be immersed in a constant-temperature bath, and to the copper tube to serve as a lead for connecting with the indicating instrument. The thermocouple can be calibrated in any convenient manner. Its construction is shown in figure 29.

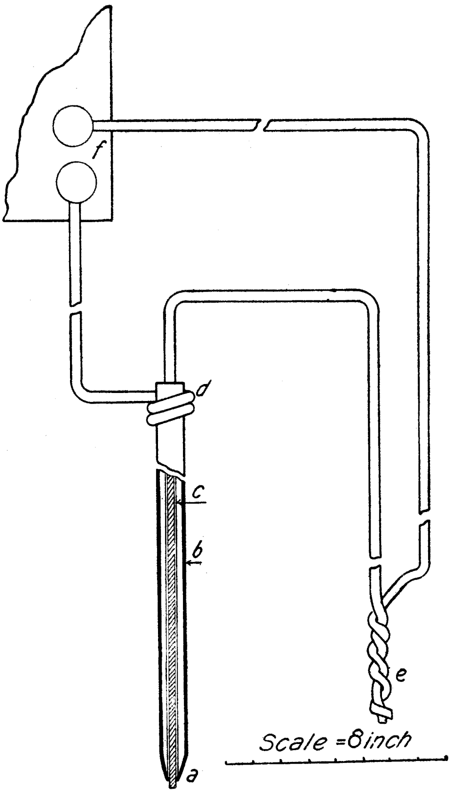

FIGURE 29.—Construction of thermocouple. *a*, Hot junction, silver soldered; *b*, copper tube; *c*, constantin wire with asbestos, cotton, or silk insulation further protected by a layer of bakelite varnish; *d*, copper lead wire, soldered on copper tube; *e*, cold junction which may conveniently be immersed in a mixture of distilled water and shaved ice, contained in a vacuum-walled bottle or tube; *f*, binding posts on indicating galvanometer or potentiometer.

STILL-HEAD.

The authors have tried various types of still-heads. At one time a column of heavy copper tubing was employed. This was thought to be satisfactory, but in one series of tests results indicated that the thermometer bulb had been heated above the normal temperature of the current of vapor on account of the transfer of heat through the walls of the still-head. This led to the development of a glass still-head which is preferable to the metal one, even if the latter caused no error through superheating.

GLASS STILL-HEAD WITH CORK CONNECTION.

For the distillation of products having maximum boiling points of 200° C. (392° F.) a still-head may be used that is attached to the copper flask by means of a cork stopper. The general design of such a still head appears in figure 27. The length indicated in this figure is usually convenient, but can be varied if desired. The cork junction can be rendered tight by luting with the litharge-glycerin mixture (see p. 16). The junction can be kept tight with this paste up to the temperatures considerably above 200° C. (392° F.), but the cork is practically reduced to coke and must be replaced by a new one for each subsequent test.

GLASS STILL-HEAD WITH METAL UNION.

After the discovery of the possibility of superheating with an all-metal still-head, a metal union was attempted by which a glass still-head could be connected with the copper flask without the use of cork or any other perishable material. A stuffing-box union and the type of still head used with it are shown in figure 28. The length of the still head can be varied according to the needs of any one test, but the size shown in the figure, which permits the use of an 8 to 9 inch column of filling material, is usually adequate.

Mounting the glass still-head in the stuffing box requires care, as the glass tube must be centered in the metal collar while soft asbestos cord saturated with a mixture of heavy oil and graphite is worked in and at intervals is compressed by screwing down a gland by means of the compression nut. This may ordinarily be done three or four times in the course of the job of putting in the packing. Once a glass still-head is mounted in a stuffing box, however, it is practically permanent, and the job need not be done over again until the still head is broken or for some other reason requires replacement. If the glass tube is approximately round, this type of junction can be made tight against any ordinary difference in pressure. The stuffing box holding the still head is attached to the copper flask by screwing on, and tightness is insured by a fiber gasket smeared with cylinder stock-graphite mixture when first put in place. The use of this lubricant prevents tearing the gasket when the joint is opened, and the same fiber gasket can be used almost indefinitely.

CONDENSER.

The authors have chiefly used condensers with glass tubes, of the type described on page 11 and shown in figure 5. A more recent design is described on page 11 and shown in figure 6. For use with a liter-charge still the condenser may be larger but the method of construction is the same.

RECEIVERS.

Several receivers have been designed to handle fractions too large for the modified Bruhl receiver (fig. 12, p. 23). The first of these was similar in design to a receiver described by Bogart[17] and worked reasonably well but was early replaced by more convenient types shown in figures 30 and 31. The first consisted essentially of a glass cylinder connecting at the bottom by means of a rubber stopper with a series of lead or tin tubes each of which was inserted through a rubber stopper into the neck of a bottle of suitable size. The distribution of fractions to the proper bottles was accomplished by the use of a rotating glass cup which had a bit of sheet iron attached to one side (fig. 30). The position of the outlet jet was changed by rotating the cup on its spindle by means of a magnet held outside the system. This device was a great improvement over anything previously used in spite of its crude construction. No attempt was made to develop it along mechanical lines because the difficulty of making the special glass cup more than neutralized the advantages of the magnetic control.

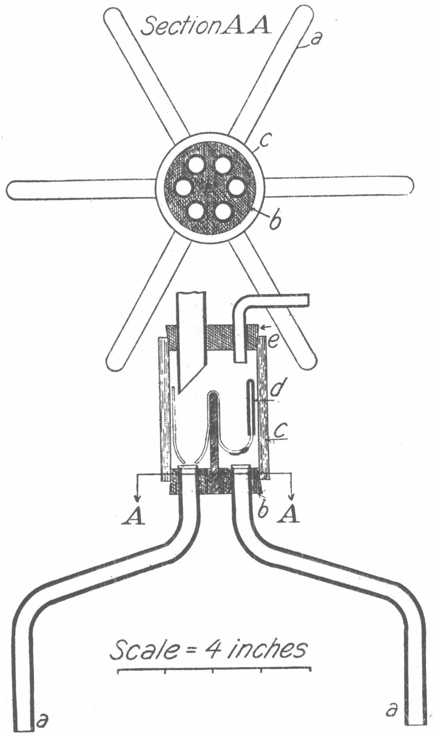

FIGURE 30.—Plan and section of magnetic distributor for vacuum distillation fractions. *a*, Tubes connecting with receiving bottles; *b*, rubber stopper holding tubes *a*; *c*, glass tube; *d*, special glass cup suspended on vertical spindle attached to stopper *b*, and with bit of sheet iron on side, which is attracted by an exterior magnet, thus rotating the cup; *e*, rubber stopper at top of tube *c* with two holes, one for condenser tube, the other for a tube connecting with manometer, vacuum pump, etc.

The type of distributor subsequently designed and constructed is shown in figure 31. This is the same general type as the magnetic device but of better mechanical design and easier to use. It consists of a top plate with a tubulature through which the condenser tube enters, a rotating spindle passing through a stuffing box, and a bottom plate that holds six tubes connecting with

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[17] Bogart, M. T., Two convenient forms of receiver for fractional distillation under diminished pressure: Jour. Ind. and Eng. Chem., vol. 7, 1915, pp. 785–786.

the various receiving bottles. As many as nine receiving tubes possibly could be attached, although this has not actually been done. Between the two plates is a glass cylinder with ground and polished ends, which can consist of the standard glass piece made for the flame type of miner's safety lamps. The cup is mounted on a spindle attached to the bottom plate and engaging with the stuffing-box spindle above. The glass cylinder is seated between the two metal plates on two rubber gaskets. The various outlets may be connected with bottles of sizes suitable for the fractions that are to be collected. Ordinary bottles up to at least one liter can be used with this apparatus.

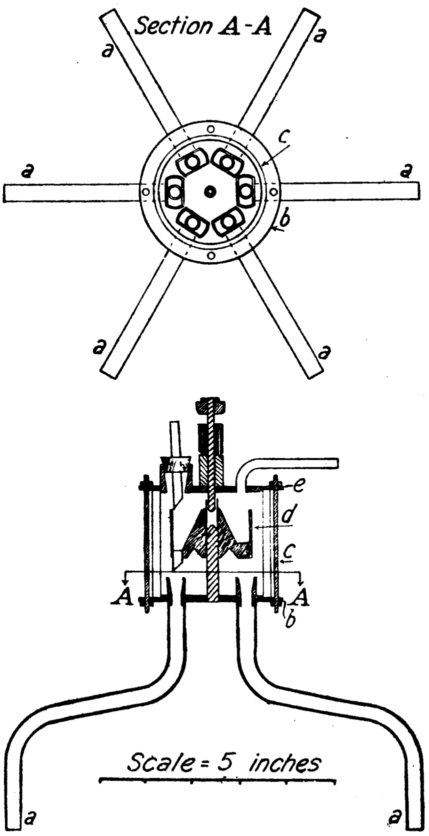

FIGURE 31.—Plan and section of manually turned distributor for vacuum distillation fractions. *a,* Tubes connecting with receiving bottles; *b,* metal bottom plate of device; *c,* glass tube; *d,* rotating metal cup mounted on spindle set in bottom plate *b* and actuated by rod passing through a stuffing box on top plate *e*; *e,* metal top plate with stuffing box, rod, and knurled head mounted in center, and openings for condenser tube and vacuum line connection off center.

ELECTRIC HEATER.

The heater used with the liter-charge still is similar to that used for the 5-gallon and 1-gallon stills (see figs. 24 and 26). The resistance element for 110-volt current contains 35 feet of No. 18 B. and S. gage nickel-chromium wire, wound in a helix on a one-fourth inch mandrel. The heating element is built according to the method described on page 56 and a wooden form of the same shape and size as the bottom of the flask is used. The supporting case extends over about three-fourths of the height of the flask and is made of two concentric cylinders of sheet metal with a 1-inch layer of broken kieselguhr brick between and with a transite gasket at the top. The space between the inner wall of the case and the flask is generally filled with asbestos rope. The heater can be controlled by a rheostat or series of rheostats with a capacity of about 8 amperes and a resistance of from 20 to 30 ohms.

STILLS FOR 500-C. C. AND 250-C. C. CHARGES.

The copper Kjeldahl flask (p. 59) is manufactured in half-liter, liter, and two-liter sizes. The dimensions of the flask neck and ring are the same in all sizes, therefore the still-head union described on page 62 can be used also with either of the smaller flasks. The apparatus described can, therefore, be modified easily to distill either 250-c. c. or 500-c. c. charges of oil in metal flasks. Practically the only part of the equipment that can not be used interchangeably with all the flasks is the electric heater. For the half-liter charge (1-liter size) flask the heating element used by the authors is the same in all details but over-all size as the one used with the liter charge still. For the 250-c. c. charge (half-liter size) flask the resistance element may be 45 feet of No. 18 (B. and S. gage) nickel-chromium wire, wound on a one-fourth-inch mandrel which is the same as the one used with the standard glass Hempel apparatus.

The authors have used for the one-half liter charge flask a heater with insulating walls the same as for the liter charge still. The heater for the copper still taking a one-half liter charge is mounted in the same way as that for the standard 300-c. c. Hempel glass flask. The method of constructing the heating element is the same for all sizes.

DEHYDRATION PRELIMINARY TO DISTILLATION.

Producing wells often yield a mixture of oil and water. Crude oil may also be contaminated with water in handling or storage. Such emulsions vary in degree of stability from physical mixtures in which the two phases can be separated by simple settling to true colloidal solutions. The stability of these emulsions is in some degree proportional to the viscosity of the oil phase, but this probably is not the only controlling factor.

A comprehensive study of the properties of different types of petroleum emulsions has not been attempted, as the present problem is to discover methods by which these emulsions can be dehydrated preliminary to analytical distillation. All possible dehydrating methods are not described—only those that have proved decidedly satisfactory in the laboratories of the bureau.

NEED FOR DEHYDRATING SAMPLES.

The analytical distillation of crude-oil samples containing more than a trace of water is undesirable on account of both the inaccuracy of the results and the difficulty during tests. Distilling a mixture of oil and water is equivalent to a steam distillation or a distillation at reduced pressure, and the results are not the same as would be obtained when distilling the oil phase in the absence of water. Furthermore, the presence of any considerable quantity of water in the distillation flask or retort is likely to cause frothing, which in turn causes unvaporized oil to be carried over into the condensing and receiving system. Also water is condensed in the still head, and when large drops have formed they are likely to fall back into the body of oil in the flask and explode with violence, as the oil is always at a temperature considerably above the boiling point of water. If the drops are large enough, the result is sure to be disastrous. The authors have seen such explosions that blew the fractionating column and thermometer out of the flask with a spray of hot oil.

With proper precaution emulsions can be distilled successfully in the conventional types of apparatus, but the procedure involved is tedious and troublesome and the results are not comparable with those obtained by distilling dry oil. Preliminary dehydration seems advisable for most samples, except nonviscous crudes containing a mere trace of water.

TYPES OF CRUDE-OIL EMULSIONS.

In the present discussion crude-oil emulsions can be divided into two classes:

1. Emulsions that do not froth when heated and that contain one per cent or less of water.
2. Emulsions that contain more than one per cent of water or that froth when heated.

The procedure for dehydrating samples of the first class has been described on page 17.

DEHYDRATION METHODS.

Four of the more promising methods for dehydrating emulsions of the second class are described below:

METHODS BASED ON SEPARATION OF OIL AND WATER BY GRAVITY SETTLING OR CENTRIFUGING.

With certain types of petroleum emulsions the oil and water phases can be separated by procedure that depends upon the difference in specific gravity between oil and water. This general method is useful for the many samples of crude petroleum that have a water layer in the bottom of the container. If this water has become mixed with the oil in the course of handling, it can be separated again by allowing the sample to stand long enough or by placing part of the mixture in a suitable container and spinning it in a centrifuge. This method is most effective with oils of low viscosity. Sometimes practically complete dehydration is effected and sometimes a partial dehydration that reduces the water content of the oil layer to one per cent or less so that it comes under class 1. Unfortunately, most emulsions do not separate in this way and the applicability of the method is limited.

METHODS INVOLVING BREAKING OF EMULSIONS AND MECHANICAL SEPARATION.

ELECTRICAL BREAKING OF EMULSIONS.

Various methods have been devised to break petroleum emulsions through the use of electricity. The Cottrell[18] method, which is largely used in certain oil fields, employs an electric current of sufficiently high voltage to cause particles of water to cohere without forming a continuous chain of drops that would cause short circuiting. This method has not been studied in detail by the authors and may or may not be capable of satisfying the requirements of preliminary dehydration of samples used in analytical distillation. The use of high-tension electric current has not seemed as practical as the method, described later, that is preferred by the authors.

The electrical method of Seibert and Brady[19] has not been tried by the authors, as it was not designed to satisfy the severe requirements of laboratory dehydration.

BREAKING EMULSIONS BY USE OF CHEMICALS.

Petroleum emulsions can sometimes be broken by using properly selected chemicals that destroy the colloidal films between particles of oil and water and thereby permit the latter to cohere in drops large enough to settle from the oil phase. This procedure is also commercially important, but the authors' tests with it have not been successful. A number of miscellaneous reagents were tried, including some of the common acids and alkalies, without complete dehydration. Also a few experiments were made with Tret-O-Lite, a patented preparation[20] that was known to have been used successfully in commercial work, but the degree of dehydration fell short of the laboratory requirements.

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[18] Cottrell, F. G., U. S. Patents 987114, Mar. 21, 1911, and 994377, June 6, 1911; Cottrell, F. G., and Speed, J. B., U. S. Patent 987115, Mar. 21, 1911; Cottrell, F. G., and Wright, A. G., U. S. Patent 987116, Mar. 21, 1911.

[19] Seibert, F. M., and Brady, J. D. Breaking up emulsions of oil and water, U. S. Patent 1290369, Jan. 7, 1919.

[20] Barnickel, W. S., Refining crude petroleum oils containing emulsified water and slimy impurities, U. S. Patent 1093098, Apr. 14, 1914. Separating naturally emulsified brine from crude petroleum, U. S. Patents 1223659–60, Apr. 24, 1917.

BREAKING EMULSIONS BY MEANS OF HEAT.

One of the largely used commercial methods of "breaking" oil-water emulsions is to heat to a moderately high temperature. This method as commercially used is likely to change the composition of the oil phase if the latter contains any appreciable content of material volatile at the temperature required to break the emulsion. The method is highly undesirable for oils containing gasoline or naphtha and has largely been superseded by more economical procedure.

However, in the laboratory it might be possible to heat and break a charge of emulsion in a closed system without permitting the volatile constituents of the oil to escape. On cooling, these constituents would condense and could be mixed again with the oil. The water should separate in drops large enough to settle out.

The authors have experimented considerably along this line. Sometimes the emulsion was run through a heated tube and collected in a receiving system equipped with a condenser that prevented the loss of volatile hydrocarbons. In other tests the emulsion was heated in an autoclave, which was allowed to cool before being opened. The temperatures to which the oil was subjected varied between 150° C. (302° F.) and 200° C. (392° F.). This treatment broke the emulsions but the drops of water apparently did not settle out of the oil layer completely. The oils after heating could be distilled without foaming but water was always present and always made trouble. This method probably would be successful with some of the less viscous types of crude but it did not dehydrate the heavy-oil emulsions with which the authors experimented. The method is useful in that it permits a preliminary partial dehydration of emulsions having a high content of water. The authors use it to remove a part of the water from emulsions containing 10 per cent or more of moisture and obtain complete dehydration by the calcium chloride method described later.

DEHYDRATION BY DISTILLATION.

Oil-water emulsions can be dehydrated by distillation under proper conditions. The general mechanism of this process is as follows:

The emulsion is heated under conditions described later that avoid the difficulties of frothing and explosive vaporization of refluxed water. The vapor containing water and volatile hydrocarbons is condensed by suitable means and the resulting distillate almost invariably collects in clean-cut layers of oil and water. These are separated by suitable means and the oil distillate can be mixed again with the cooled unvaporized oil. The product is identical with the original oil phase of the emulsion, provided the distillation has not been conducted at a temperature high enough to cause cracking. The authors' experience as well as that of other operators has indicated that the maximum temperatures necessary to vaporize the water in a petroleum emulsion are considerably lower than the temperatures at which cracking occurs. Some of the commercial processes cause cracking intentionally in order to increase the gasoline content of the oil.

The laboratory problem is to find a means of distilling the emulsion that avoids frothing and refluxing of water. Three procedures have been used.

DISTILLING FROM FLASKS OR RETORTS WITH HEATED FRACTIONATING COLUMNS.

The froth or foam produced by heating an emulsion of water and a viscous oil can be destroyed readily by moderate superheating. Water will not reflux from a fractionating column that is hotter than 100° C. (212° F.). Emulsions can be distilled from flasks or retorts when the still head or fractionating dome is heated to a moderately high temperature. This procedure is very common in petroleum laboratories, the general method of operation being to heat the mass of oil very slowly and gradually in the body of the flask or still and to play a flame on the neck of the flask or dome of the still. This procedure is far from fool-proof, but it is an effective means for complete dehydration.

CONTINUOUS DISTILLATION METHODS.

Some of the most successful commercial methods of distilling emulsified crudes involve the use of so-called "pipe stills," through which the oil-water mixtures are passed continuously. The volume of oil in the heated zone is never sufficient to permit frothing over into the vapor line, and probably the temperatures carried are usually high enough to prevent frothing. This general principle has also been used in the design of laboratory apparatus. In a promising type the procedure involves passing a slow stream of oil through a furnace tube equipped with an internal spiral that retards the flow and promotes thorough heating.

DISTILLING UNDER PRESSURE.

If oil-water emulsions are distilled under very moderate pressures above atmospheric, the tendency to froth or foam is reduced. The authors have thought that a suitably constructed still and condenser capable of withstanding pressures such as might develop in heating a charge of crude oil up to about 200° C. (392° F.) might serve as a convenient device for dehydrating samples. A number of stills of this type have been constructed and tried, but with no success so far. Work along this line for the present at least has been abandoned, not because the authors are convinced that this general procedure can not be used but because experience has indicated that dehydration with calcium chloride is satisfactory.

DEHYDRATION BY MEANS OF CHEMICAL REAGENTS.

Crude-oil emulsions can not usually be dehydrated by means of chemical reagents by any simple process of agitation. Most of the samples that have been received in the laboratories of the bureau were too viscous at ordinary temperatures to permit thorough mixing with either solid or liquid reagents. Moreover, it seems that oil, and not water, is generally the external or dispersing phase in petroleum emulsions, which means that dehydrating reagents, even if thoroughly mixed, are likely to be ineffective unless they have the power of "breaking" the emulsion as well as absorbing the water.

The authors have broken emulsions easily by heating samples in an autoclave up to a temperature not exceeding 200° C. (392° F.). This breaking did not insure complete settling out of the water, but a suitable dehydrating agent was placed in the autoclave in the belief that the water could be taken up completely and quantitative separation effected. The dehydrating agent selected should have no chemical action on the oil and should not be appreciably soluble in the oil either in its anhydrous or hydrated form. It should have a specific gravity high enough to settle readily from the oil and should retain its affinity for water up to about 200° C.

Several reagents, theoretically promising, proved unsatisfactory when tried. No extensive investigation was made to ascertain whether or not the difficulties encountered could be obviated, as the tests with ordinary fused calcium chloride were entirely successful. Even if the plaster of Paris, lime, anhydrous copper sulphate, and other reagents had worked equally well the calcium chloride would have been preferred because of its cheapness and availability. Lime, CaO, is cheap but can not easily be kept without deterioration; moreover, the authors were unsuccessful in dehydrating oil with it.

According to textbooks of inorganic chemistry[21] calcium chloride forms a hydrate with six molecules of water which when heated to 200° C. loses four and retains two molecules of water. The di-hydrate $CaCl_2.2H_2O$ is, therefore, stable at all temperatures below 200° C., and as it contains 3.1 parts by weight of anhydrous calcium chloride for each part of water, in treating oil a quantity of $CaCl_2$ must be used equivalent to approximately 3 grams for each cubic

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[21] Roscoe, H. E., and Schorlemmer, C.: Treatise on chemistry, vol. 2, 1907, pp. 529–530.

centimeter of water contained by the charge of oil. The authors have been able to use a slightly smaller proportion of calcium chloride successfully but regard the figure given as best for general use.

Calcium chloride is nonvolatile and no harm would be done for present purposes if a moderate proportion dissolved in the oil in the course of treatment. Even though treatment with this reagent apparently could not alter the distillation range of oil, the amount dissolving or held in suspension was ascertained. The solution of calcium chloride would affect the specific gravity of the oil phase of an emulsion, measurement of which is frequently desired.

Determinations were made of the amount of calcium chloride present in several samples of oil that had been dehydrated by means of this reagent. In some tests the oil was extracted thoroughly with water and the amount of calcium determined by precipitating as the oxalate and weighing as the oxide. In other tests samples of treated oil were ashed and the total ash regarded as calcium chloride. Results of both methods showed that the amount of calcium chloride dissolved was only 0.1 per cent, which is about the same as the usual experimental error in making specific gravity determinations. The solubility is, therefore, so slight as to be negligible.

A question might be raised regarding possible cracking produced by heating oil in an autoclave with $CaCl_2$ up to 200° C. This temperature is usually regarded as well below the lower limit of cracking for hydrocarbon oils, but the authors decided to obtain direct evidence on the subject. The distillation range of several anhydrous samples was determined and portions of these same oils were heated in the presence of $CaCl_2$ to 200° C. in an autoclave cooled and subjected to the distillation test. No change occurred, which proved nonoccurrence of cracking. The fact that the autoclave after cooling showed no residual pressure was also evidence that cracking did not occur. When an oil is cracked some permanent gas is always formed, and if the quantity were appreciable the cooled autoclave would be under pressure.

QUALITATIVE TEST FOR WATER.

The presence of water in a sample of crude oil can always be determined by attempting to make a distillation. Generally, however, the possibility of water in a sample can be predicted without setting up apparatus for a distillation for proof.

Place from 20 to 50 c. c. of the suspected oil in a 100-c. c. Erlenmyer flask and warm gently, preferably on an electric hot plate. If the oil swells up or froths on heating, water is present in finely divided condition and the sample should be dehydrated by a suitable method. If the oil does not froth but droplets of moisture condense on the walls or neck of the flask, dehydration is still necessary.

QUANTITATIVE TEST FOR WATER.

If either foaming or condensation of water on the flask neck is observed, the next step is to ascertain the actual percentage of moisture present in the oil. This can be done best by the distillation method, a convenient modification of which is described.[22]

The apparatus (see fig. 32) needed consists of a source of heat, preferably an electric heater of special design, but if desired a gas burner or alcohol lamp can be used; a 500-c. c. round-bottomed short-necked glass flask; a "distilling-tube receiver"; and a condenser of the size and type shown in the figure.

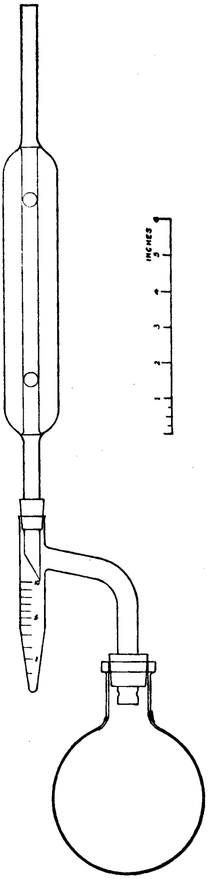

FIGURE 32.—Assembly of glass parts of apparatus for quantitative determination of water in an emulsion.

The reagent used is a mixture composed of 80 parts by volume of commercial xylol and 20 parts by volume of commercial 90 per cent benzol, or, preferably, a petroleum naphtha satisfying the following requirements when distilled in the official A. S. T. M. apparatus:

Five per cent mark not below 90° C. (194° F.) nor above 100° C. (212° F.).

Ninety per cent mark not above 195° C. (383° F.).

Place 100 c. c. of the emulsion to be tested in a graduate and measure out 100 c. c. of solvent. Pour the emulsion into the 500-c. c. flask and drain for a minute or two. Then wash all the emulsion out of the graduated cylinder, using successive parts of the measured 100 c. c. of solvent. Drop a boiling stone, a bit of unglazed porcelain, into the flask. Connect with the distilling-tube receiver and the condenser; be sure that the ground tip of the latter is placed so that drops of condensate must fall into the receiving graduate and not into the side tube, also that the position of the diagonally ground tip is approximately as indicated in figure 32.

Heat until the distillation proceeds at the rate of 2 to 4 drops a second, observe the rate of fall from the ground tip of the condenser, and establish the degree of heat necessary to maintain this rate. Allow the distillation to continue until all droplets of water in the flask, the distillation tube,

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[22] Dean, E. W., and Stark, D. D., A convenient method for the determination of water in petroleum and other organic emulsions: Jour. of Ind. and Eng. Chem., vol. 12, 1920. pp. 486–490.

and the condenser have disappeared. This usually takes less than an hour and in routine work the distillation can be started and left for an hour, when the final readings are made. If a ring of droplets of water is observed in the condenser tube, the rate of distillation should be increased for a few minutes so that the vapor level on the condenser tube is raised slightly, thereby sweeping off the water. The rate of distillation can be increased by applying more heat or by placing an insulating shield of asbestos paper over the flask. A ring of water generally does not form if the condenser tube is clean.

The heat is then turned off and the distilling flask disconnected. The latter need not be cooled if care is taken not to let the escaping vapor ignite. A drop of water sometimes hangs on the ground tip of the condenser, but nearly always falls off when the graduated receiver is detached from the condenser.

The volume of water collected in the graduated receiver is then read, with the tube held in a vertical position. The receiver is then emptied and dried and is ready for another determination. The flask is usually set aside to cool and another flask, previously cleaned and dried, is used for the next determination.

INTERPRETATION OF RESULTS OF PRELIMINARY TESTS.

If the oil does not froth on preliminary heating, and if its water content is less than 1 per cent, it belongs to Class 1 and can be dehydrated by the procedure described on page 17. If the oil froths, or if it contains more than 1 per cent of water, it should be dehydrated by some suitable method. The authors prefer the use of an autoclave and calcium chloride.

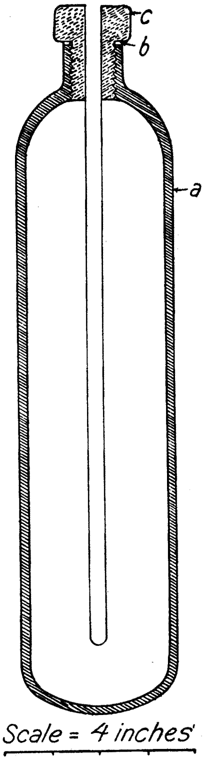

FIGURE 33.—Section of autoclave for dehydrating petroleum emulsions by heating under pressure with fused calcium chloride. *a*, Body of autoclave, a remodeled one-liter size oxygen cylinder; *b*, fiber gasket; *c*, brass plug with brazed-in thermometer well.

DEHYDRATION OF CRUDE OIL IN AN AUTOCLAVE WITH CALCIUM CHLORIDE.

APPARATUS.

An autoclave of about one liter capacity, capable of withstanding a pressure of 300 pounds a square inch, and equipped with a thermometer well. The authors have used several autoclaves. The first was made by welding a top and bottom into a piece of nominally 3-inch extra-heavy iron pipe and threading and machining a hole in which the plug and thermometer well were inserted. A more satisfactory device, shown in figure 33, was made of a one-liter cylinder originally used as a container for oxygen in one of the standard sets of breathing apparatus for mine-rescue work. The neck was machined to take a plug with straight-cut threads seating on a fiber gasket. The plug carries a thermometer well. The plug and well can be machined or bored out of a single piece of brass or built of several parts and brazed together.

A supporting stand and source of heat. The former may be a conventional ring stand, the latter any good type of large laboratory burner.

A thermometer reading up to 200° C. (392° F.).

A mechanical shaking machine. The type used by the authors is a stock article obtained from one of the chemical supply houses, and is moderately satisfactory. Many other good devices are without doubt available in the market, or if desired a satisfactory shaker could be easily improvised.

REAGENT.

Ordinary commercial fused calcium chloride screened to remove all powder and lumps passing a sieve of one-fourth-inch mesh is used for the reagent. A granular type of calcium chloride, which is generally labeled "anhydrous" and is largely employed for drying gases, is not recommended, as it is likely to be the dehydrate, $CaCl_2.2H_2O$.

PROCEDURE.

Place in the autoclave approximately half a liter of oil and a quantity of calcium chloride equivalent to 3 grams for each cubic centimeter of water contained in the oil. For example, if the oil has been shown to contain 3 per cent of water, the total amount of water in the charge of oil is 15 c. c. and 45 grams of calcium chloride is required. If the water content of the emulsion has not been determined, it may be assumed to contain no more than 5 to 7 per cent, and a fixed quantity of 100 grams of calcium chloride can be used. There seems to be no objection chemically to using a reasonable excess of this reagent, and as it is cheap, expense is not important. More than 7 per cent of water may be present, in which case the quantity of dehydrating agent will prove insufficient, but this risk must be incurred if a preliminary quantitative determination is not made.

Heat until the thermometer placed in the well reads approximately 200° C. (392° F.). Remove the thermometer and place the autoclave on the rack of the shaking machine. Shake vigorously for at least five minutes. Remove from the shaking machine, place in a vertical position and allow to cool. To save time the hot autoclave can be immersed in a bucket of water. After it is thoroughly cooled unscrew the plug and withdraw a suitable charge of oil. This should preferably be done with a pipette or siphon, although it may be poured out. The oil should be absolutely dehydrated and can be subjected to fractional distillation without further treatment. If a specific-gravity determination is made, 0.001 should be deducted from the apparent figure to correct for the small amount of dissolved calcium chloride.

If the oil treated is thought to have a relatively high gasoline content, after the autoclave has cooled it may again be placed on the shaking machine and agitated for two or three minutes. This insures homogeneity of the oil, as otherwise the surface film might be richer in gasoline than the rest because of gasoline vapor that condensed on cooling and did not have a chance to mix thoroughly with the body of oil.

This method of dehydration has been used extensively by the authors and has been found more satisfactory than any other method tried. It is subject to certain obvious objections, and the authors have never been convinced that there is not a better way of extracting water quantitatively from petroleum emulsions. The present description is offered as a record of the bureau's experience to date and with the hope that if the method suggested does not prove acceptable to other laboratories the general information supplied will lead to the development of more satisfactory procedure.

APPENDIX.

TABLE 8.—*Equivalent centigrade and Fahrenheit readings.*

°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
0	32	50	122	100	212	150	302	200	392	250	482	300	572
1	34	1	124	1	214	1	304	1	394	1	484	1	574
2	36	2	126	2	216	2	306	2	396	2	486	2	576
3	37	3	127	3	217	3	307	3	397	3	487	3	577
4	39	4	129	4	219	4	309	4	399	4	489	4	579
5	41	5	131	5	221	5	311	5	401	5	491	5	581
6	43	6	133	6	223	6	313	6	403	6	493	6	583
7	45	7	135	7	225	7	315	7	405	7	495	7	585
8	46	8	136	8	226	8	316	8	406	8	496	8	586
9	48	9	138	9	228	9	318	9	408	9	498	9	588
10	50	60	140	110	230	160	320	210	410	260	500	310	590
1	52	1	142	1	232	1	322	1	412	1	502	1	592
2	54	2	144	2	234	2	324	2	414	2	504	2	594
3	55	3	145	3	235	3	325	3	415	3	505	3	595
4	57	4	147	4	237	4	327	4	417	4	507	4	597
5	59	5	149	5	239	5	329	5	419	5	509	5	599
6	61	6	151	6	241	6	331	6	421	6	511	6	601
7	63	7	153	7	243	7	333	7	423	7	513	7	603
8	64	8	154	8	244	8	334	8	424	8	514	8	604
9	66	9	156	9	246	9	336	9	426	9	516	9	606
20	68	70	158	120	248	170	338	220	428	270	518	320	608
1	70	1	160	1	250	1	340	1	430	1	520	1	610
2	72	2	162	2	252	2	342	2	432	2	522	2	612
3	73	3	163	3	253	3	343	3	433	3	523	3	613
4	75	4	165	4	255	4	345	4	435	4	525	4	615
5	77	5	167	5	257	5	347	5	437	5	527	5	617
6	79	6	169	6	259	6	349	6	439	6	529	6	619
7	81	7	171	7	261	7	351	7	441	7	531	7	621
8	82	8	172	8	262	8	352	8	442	8	532	8	622
9	84	9	174	9	264	9	354	9	444	9	534	9	624
30	86	80	176	130	266	180	356	230	446	280	536	330	626
1	88	1	178	1	268	1	358	1	448	1	538	1	628
2	90	2	180	2	270	2	360	2	450	2	540	2	630
3	91	3	181	3	271	3	361	3	451	3	541	3	631
4	93	4	183	4	273	4	363	4	453	4	543	4	633
5	95	5	185	5	275	5	365	5	455	5	545	5	635
6	97	6	187	6	277	6	367	6	457	6	547	6	637
7	99	7	189	7	279	7	369	7	459	7	549	7	639
8	100	8	190	8	280	8	370	8	460	8	550	8	640
9	102	9	192	9	282	9	372	9	462	9	552	9	642
40	104	90	194	140	284	190	374	240	464	290	554	340	644
1	106	1	196	1	286	1	376	1	466	1	556	1	646
2	108	2	198	2	288	2	378	2	468	2	558	2	648
3	109	3	199	3	289	3	379	3	459	3	559	3	649
4	111	4	201	4	291	4	381	4	471	4	561	4	651
5	113	5	203	5	293	5	383	5	473	5	563	5	653
6	115	6	205	6	295	6	385	6	475	6	565	6	655
7	117	7	207	7	297	7	387	7	477	7	567	7	657
8	118	8	208	8	298	8	388	8	478	8	568	8	658
9	120	9	210	9	300	9	390	9	480	9	570	9	660

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INDEX.