APPARATUS AND METHODS FOR THE SEPARATION, IDENTIFICATION, AND DETERMINATION OF THE CHEMICAL CONSTITUENTS OF PETROLEUM

By Edward W. Washburn, Johannes H. Bruun, and Mildred M. Hicks

ABSTRACT

This paper contains a description of the following apparatus and methods:

1. A rectifying still with a 20-plate column and with means for independently controlling and measuring the temperatures of the plates. The still is designed for distillation in a stream of an inert gas (CO_2) with or without boiling.

2. All-glass rectifying stills for vacuum distillation. They are heated by immersion in an electrically heated bath of nickel shot.

3. Various types of molecular stills by means of which distillation can be carried out at any temperature at which the vapor pressure at the distilling surface is not lower than the degree of vacuum attainable.

4. Methods and apparatus for fractionation by crystallization or melting.

5. An apparatus for combustion analysis, with special provisions for purifying the oxygen employed and with all rubber connections eliminated. With the aid of this apparatus the formula for any hydrocarbon up to C_{100} can be determined.

The change in the iodine number of a petroleum oil produced by heating it for different periods and at different temperatures up to 370° C. in (*a*) air and (*b*) H_2, N_2, and CO_2, respectively, has been determined, and it is shown that in the absence of air this change is greatly reduced.

Evidence is presented showing that the hazards from exposed mercury surfaces in a laboratory are eliminated as soon as the mercury surface becomes contaminated with a continuous layer of a heavy oil or grease.

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PART 1

I. INTRODUCTION

By Edward W. Washburn

In cooperation with the American Petroleum Institute, the Bureau of Standards is conducting an investigation, the object of which is the development of methods for fractionating petroleum into its chemical constituents and for identifying these constituents. An examination of the literature on the composition of petroleum discloses the reported existence of a large number of different hydrocarbons to which formulas and values of physical properties have been assigned. A study of the evidence presented in identification of these "compounds," however, impresses one chiefly because of its inadequacy. In fact, with the exception of some of the lower boiling constituents, most of the compounds whose existence has been reported must be classed as purely fictitious in the light of the evidence at present available.[1]

Most of the previous work on the problem of the constitution of petroleum has rested almost entirely upon the results of fractional distillation, a process which is in many instances inadequate for effecting complete separation of the mixture into its constituents. In attacking the problem anew it was decided to fractionate by both distillation and crystallization, so that constant boiling mixtures might be broken up by crystallization and constant freezing mixtures by distillation. In this way complete separation can ultimately be

[1] See, for example, Burrell, Ind. Eng. Chem., **20**, p. 602; 1928.

attained. The purpose of the present paper is to describe the apparatus and methods employed.

In undertaking the present investigation it was decided to take advantage of the initial fractionation resulting from a commercial straight-run distillation of a petroleum sample from a single pool. Since the lower boiling fractions of such a distillation have been investigated to some extent by other investigators, it was decided to start the present work with what is known commercially as the gas-oil fraction. Through the courtesy of Dr. W. Van Der Gracht, of the Marland Oil Co., of Oklahoma, a petroleum sample from the Oklahoma field was subjected to a straight-run distillation, and all of the fractions resulting therefrom were sent to the bureau. The general characteristics of these fractions are presented in Table 1.[2]

TABLE 1.—*Distillation of petroleum from No. 6 well of the South Ponca Field, Kay County, Okla.*

WILCOX SAND

Property	Naphtha		Kerosene	Gas oil [1]	Wax distillate	Bottoms (color, brown)
Yield ---- per cent	16.4	22.9	15.4	16.0	18.1	10.2
Gravity ---- °API	64.8	52.0	41.5	34.6	29.1	18.1
Boiling point:						
Initial ---- °F	126	214	----	----	----	----
End ---- do	358	436	----	----	----	----
Flash point ---- do	----	----	158	225	325	545
Fire point ---- do	----	----	180	275	390	620
Saybolt sec	----	----	----	----	106 at 100° F.	207 at 210° F.
Congelation ---- °F	----	----	----	----	80	92

[1] Contained 0.28 per cent S.

The first step in the further fractionation of the gas-oil fraction required a still of such capacity as to necessitate construction from metal. It was impossible to carry out the distillation by boiling under atmospheric pressure, since decomposition occurs at the temperatures required. The usual recourse under such circumstances is to employ vacuum distillation. A vacuum distillation, however, possesses certain disadvantages. In the first place the lowest boiling fraction contains hydrocarbons which are gases at ordinary temperatures and pressures, and this fraction would be lost in a vacuum distillation unless a collecting pump were employed. In the second place it is difficult to construct a still with gasket connections, for operation at relatively high temperatures, which will remain absolutely vacuum tight throughout the considerable period of time covered by the distillation. The presence of very slight leaks would, it is true, not interfere with the maintenance of the necessary vacuum, since the vacuum pump could easily take care of them. Such slight leaks,

[2] Since the receipt of this material a second lot of 1,000 gallons from the same well has been obtained and 500 gallons are to be subjected to a commercial straight-run low-temperature distillation with 2 per cent cuts. Work upon the further fractionation of the lowest boiling of these fractions is now under way.

however, whose presence would be difficult to detect during the distillation, would result in the introduction of traces of oxygen into the still, and oxygen has a pronounced effect in promoting the cracking of hydrocarbon vapors at high temperatures.

In order, therefore, to avoid the use of vacuum distillation, it was decided to carry out the process in a series of isothermal steps in each of which the temperature of the liquid in the still pot is kept constant (and low enough to avoid cracking) while distillation is compelled to proceed by passing through the liquid a fine stream of bubbles of previously heated oxygen-free carbon dioxide. Then, after passing through condensers, this carbon dioxide is absorbed by a solution of KOH, above which remains the fraction composed of the uncondensed hydrocarbon gases. Previous studies, described below, demonstrated that under these conditions cracking is reduced to a minimum. Obviously, in this process the pressure both inside and outside the still is approximately atmospheric, being slightly higher on the inside so that no leakage into the still can occur.

In constructing the still it was decided to provide the plates in the rectifying column with separate heaters and thermocouples so that the temperatures of these plates could be independently controlled and measured.

PART 2

II. A RECTIFYING STILL FOR DISTILLATION IN A CURRENT OF INERT GAS

By Johannes H. Bruun and Mildred M. Hicks

1. THE DISTILLATION TRAIN

The elements of the train will be described in the order of passage of the inert gas from its storage cylinder to its final absorption. (See fig. 1.)

(*a*) The Purification Train.—The CO_2 from its storage cylinder, *1*, passes first through two drying tubes, *2*, filled with "dehydrite" ($MgClO_4.3H_2O$), then through a flow meter, *3*, into a pyrex glass tube, *4*, filled with copper shavings and heated electrically to 650° C. Glass or copper-to-glass seals are used for all connections in this part of the train.

(*b*) The Manometer and Safety Valves.—The CO_2 from the furnace tube passes first through a cooling coil and then past a mercury manometer, *5*, provided with a safety valve, *6*. (For details, see fig. 2.) This manometer registers the total pressure of the gas, which in turn is determined by the depth of liquid in the still pot plus that on the plates of the rectifying column.

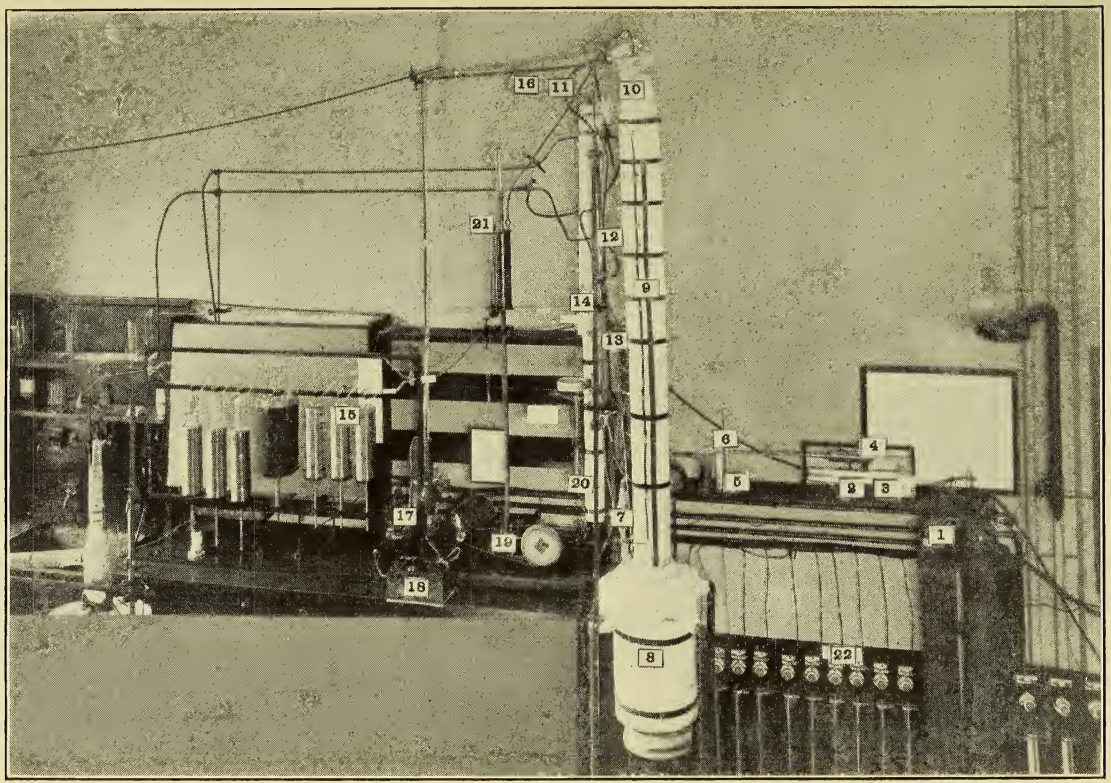

FIG. 1.—*Rectifying-still assembly*

The safety valve acts with either increase or decrease of pressure to prevent any access of air to the gas stream. An automatic shut-off valve prevents any possible back flow of liquid from the still in the event of accidental interruption of gas pressure.

The CO_2 enters the still pot at *7*, first passing through a copper tube provided with an electrical heating coil. At the bottom of the still pot this tube is bent to form a large ring which is perforated so as to break up the gas flow into numerous streams of fine bubbles.

(*c*) The Still Pot (*8* in fig. 1. For detail, see fig. 3).—The pot holds about 20 liters. It is made of welded steel and is joined to the column by a reinforced bolted flange sealed with a copper-ring gasket. The pot is heated by three independent electric heaters, one at the

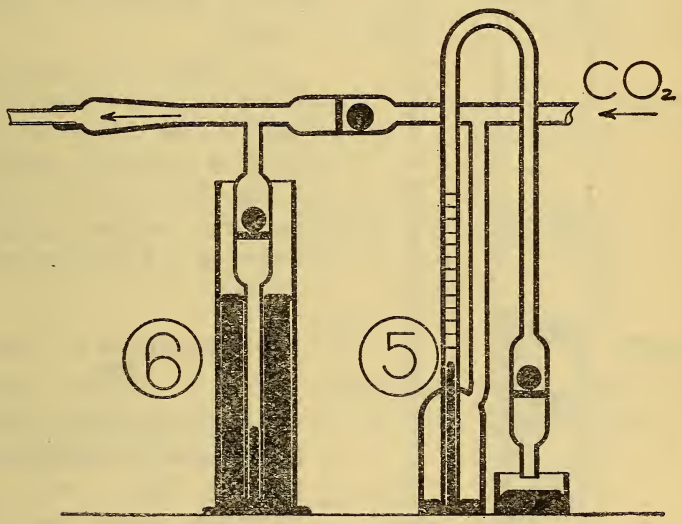

Fig. 2.—*Manometer and safety valve*

bottom and two coiled around the cylinder. A thermocouple is located about 2 inches above the bottom of the pot.

(*d*) The Fractionating Column.—The column, *9*, contains 20 plates. Each plate is provided with an independent heating coil and alternate plates with thermocouples. These heating coils, together with the insulating covering of the column, serve to maintain the desired temperature conditions in the column and make it possible to clear the column at the end of the distillation. The top of the column contains a reflux condenser, *10*, the temperature of which (as indicated by a thermocouple) is controlled by circulating oil from a special heating and pumping system, *14*, *20*, *19*, and *21*.

(*e*) The Condensers.—The gas and vapor stream, after leaving the column, passes around a well containing a thermocouple and enters the first condenser, *12*, through a copper tube, *11*, provided with a heating coil to prevent the formation of a solid condensate.

This tube is connected by a copper-to-glass seal to the inner tube of a vertical Liebig condenser, cooled by air or water of controlled temperature. (For detail, see fig. 3.) The condensate from this condenser is received in the graduated tube, *13*, from the top of which the gas stream passes first through a water-cooled condenser, *15*, and then through a series of condensers of decreasing temperatures as follows: 0°, −15°, and −80° C.

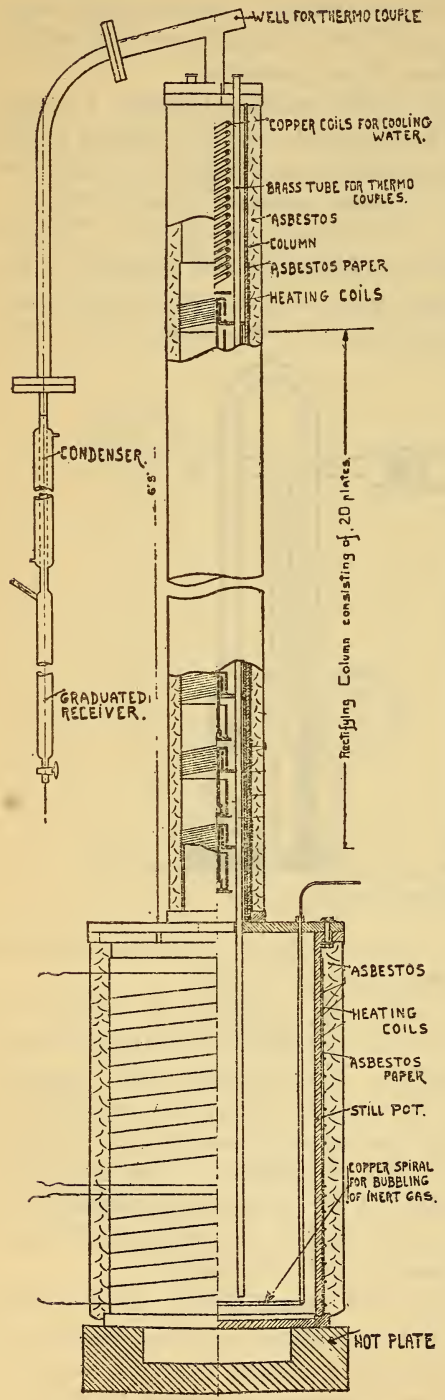

FIG. 3.—*Rectifying-still detail*

(*f*) THE CO_2 ABSORBERS.—From the last condenser of the train the gas passes through a series of saturated solutions of KOH which absorb the CO_2, and the residual gases are collected in bottles over KOH solution.

2. DISTILLATION OF THE GAS OIL

Before charging the still it was first assembled and tested for leaks by filling it with CO_2 at 25 pounds pressure and allowing it to stand for 15 days. At the end of this time the gauge showed a pressure of 25 pounds. The still pot was then charged with gas oil to about three-fourths of its capacity. A stream of dry oxygen-free CO_2 at the rate of 150 cm^3 per minute was first bubbled through the oil for five hours at room temperature in order to remove dissolved air and water. The temperature of the still pot was then gradually raised until all of the plates of the column were filled as shown by the reading

of the manometer. (Fig. 2.) The heating coils of the plates were then adjusted so as to give a controlled gradient of about 70° C. between the bottom and top plates of the column. The temperature of the reflux condenser was set about 2° lower than the temperature of the upper plate. As distillation proceeded, the temperature of the still pot was raised from time to time, with corresponding adjustments of the column, until the temperature of the liquid in the pot reached 350° C. The column was then cleared by gradually raising the temperature of the plates in succession, beginning with the lowest one. Table 2 gives the results of the distillation.

TABLE 2.—*Distillation data*

Serial number of fraction	Time	Temperature, top of column	Temperature, bottom of column	Volume of fraction
	H. *M.*	°*C.*	°*C.*	*cm*³
3	6 --	107 to 221	About 306	910
4A	10 20	222 to 232	307 to 312	910
4B	13 40	233 to 237	313 to 316	565
5	16 40	238 to 252	317 to 321	845
6	19 --	253 to 267	322 to 327	875
7	20 --	268 to 274	328 to 330	860
8	23 --	275 to 279	330 to 335	860
9	31 --	280 to 285	336 to 344	890
10	32 20	286 to 301	345 to 351	910
Bottoms				7,800

PART 3

III. THE EFFECT OF HIGH TEMPERATURES UPON PETROLEUM IN THE PRESENCE OF HYDROGEN, NITROGEN, OR CARBON DIOXIDE

By Johannes H. Bruun

Before the selection of carbon dioxide as the inert gas for use in the distillation procedure just described, experiments were made with different inert gases to determine the effects of these gases upon the tendency of the oil to crack at the temperatures employed in the distillation.

These experiments were carried out in the apparatus shown in Figure 4. The entire assembly is made of pyrex glass. The gas employed is first purified, preheated, and then passed continuously into the oil, which is heated to definite temperatures for different intervals of time. The amount of cracking is estimated by comparing the iodine numbers of the oil before and after subjecting it to this treatment. The inert gas passes from its storage cylinder through a drying tower, *1*, filled with magnesium perchlorate trihydrate and then into an electrically heated furnace, *2*, containing copper shavings for the removal of oxygen (temperature 650° C.).

A cooling coil, *5*, is placed next in the train, and this is followed by a second drying tube, *6*. The gas is then preheated, *7*, and bubbled into the flask containing the oil in contact with copper and brass turnings. A mercury-seal safety valve, *8*, is placed between the heater and the flask, thus taking care of any excess pressure.

The inert gas is first allowed to bubble through the oil at room temperature for two hours in order to free it from dissolved or occluded gases or water vapor. The temperature is read from a thermometer suspended in the flask. The flask is provided with a reflux column kept at room temperature, using an air blast when necessary. A cotton-filled bulb in the gas outlet at the top of the column frees the gas from any oil spray, and the gas is then forced

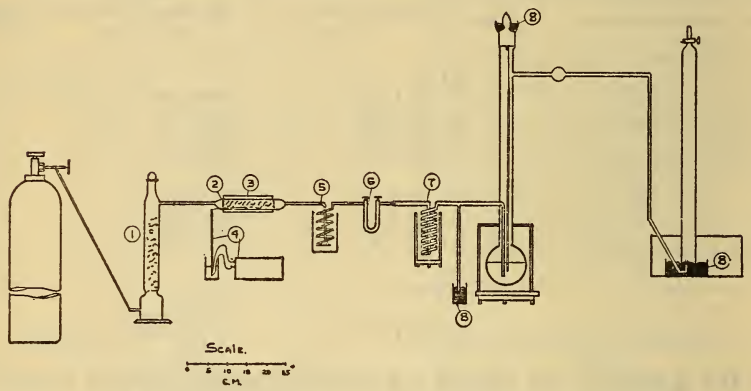

FIG. 4.—*Apparatus for studying cracking behavior*

1, Drying jar with Mg perchlorate trihydrate; *2*, copper tube filled with copper shavings; *3*, electrical heating coils; *4*, potential meter and thermocouple; *5*, cooling coils; *6*, drying tube; *7*, preheater; *8*, mercury seal

through a mercury seal. The hydrogen and nitrogen are allowed to escape, but the carbon dioxide is absorbed in a tower filled with a saturated solution of potassium hydroxide. Using the "wax distillate" from the original distillation (see Table 1), the following results were obtained (Table 3):

TABLE 3.—*Cracking behavior of raw-wax fraction in the presence of various gases*

[EFFECT OF NATURE OF GAS—THREE HOURS' HEATING AT 370° C.

Gas	Iodine number		
	Before	After	Increase
N_2	16.0	17.5	1.5
H_2	16.0	17.4	1.4
CO_2	16.0	17.2	1.2

TABLE 3.—*Cracking behavior of raw-wax fraction in the presence of various gases* —Continued

EFFECT OF CO_2—VARIATION WITH TIME OF HEATING AT 370° C.

Time (hours)	Iodine number		
	Before	After	Increase
0.5	16.0	16.4	0.4
3	16.0	17.2	1.2
20	16.5	21.5	5.0

EFFECT OF CO_2—VARIATION WITH TEMPERATURE FOR A 20-HOUR HEATING PERIOD

t (° C.)	Iodine number		
	Before	After	Increase
100	16.5	16.6	0.1
200	16.1	16.1	.0
250	16.7	16.8	.1
315	16.4	16.8	.4
350	16.7	19.4	2.7
370	16.7	21.5	5.0

EFFECT OF BOILING IN CONTACT WITH AIR FOR 20 HOURS WITH A RETURN CONDENSER

B. p. (° C.)		Iodine number		
Initial	After 20 hours	Initial	After 20 hours	Increase
370	330	16.3	59.1	42.8

TABLE 4.—*Cracking behavior of refined wax*[1] *(containing 0.09 per cent sulphur) in the presence of CO_2 during 20 hours' heating at various temperatures*

t (° C.)	Iodine number		
	Before	After	Increase
200	11.4	11.5	0.1
250	11.4	11.4	.0
320	11.4	11.5	.1
360	11.4	16.7	5.3

[1] The raw-wax fraction contained 0.28 per cent S. After washing with concentrated H_2SO_4 this was reduced to 0.09 per cent. At the same time the iodine number fell from 16 to 11.4.

From these results it is clear that in the presence of these inert gases little change in iodine number occurs during prolonged heating up to 320° C., and even at 370° the iodine number increases only one unit at the end of three hours' heating.

PART 4

IV. GLASS RECTIFYING STILLS FOR VACUUM DISTILLATION

By Johannes H. Bruun

The fractions obtained from the disillation in the large still are listed above in Table 2. The next step in the fractionation is to subject these fractions to further distillation in vacuo. For this purpose a series of all-glass stills of successively decreasing size is employed. These stills are all of the same general type which is shown in Figure 5. The rectifying column is vacuum or air jacketed and packed with steel "jack chain."[3]

The air jackets are provided with external heating coils to control the reflux. Thermometers or thermocouples are used for indicating the temperatures of the still pot and of the top of the column. A filling tube permits intermittent feeding of liquid into the still pot without breaking the vacuum and, by closing the stopcock and admitting CO_2 to the receiver and condenser, fractions can be withdrawn from the receiver without breaking the vacuum in the still proper. All stopcocks are partially sealed with mercury seals, and the still is heated by an electrically heated bath of nickel shot. This bath is a good heat conductor, does not oxidize or smoke, and at any time can be rapidly cooled by means of an air blast. The still is connected through a liquid-air trap and an intermediate ballast (a 3-liter flask) to a mercury diffusion pump and McLeod gauge.

For each fraction at least three of the following properties are determined—density, initial freezing point, initial boiling point, refractive index, viscosity—and on the basis of these properties the fractions are combined for further fractionation by distillation, crystallization, or melting. A series of flow charts (illustrated in fig. 6) is kept, showing the complete fractionation history of each fraction. Up to date (August, 1928) the original 15-liter gas-oil fraction has been separated into over 600 different fractions.

A preliminary combustion analysis and molecular weight determination on one of the still impure fractions (fig.15) indicated an empirical formula in the neighborhood of $C_{18}H_{36}$.

PART 5

V. MOLECULAR STILLS

By Edward W. Washburn

The higher melting paraffin waxes can be heated without decomposition only to temperatures at which their vapor pressures are very small. With the usual types of vacuum stills it has not generally been considered feasible to make separations at vapor pressures below a few millimeters; but many substances, which ordinarily are not distilled

[3] Dean, Hill, Smith, and Jacobs, Bureau of Mines, Bulletin 207, p. 9; 1922.

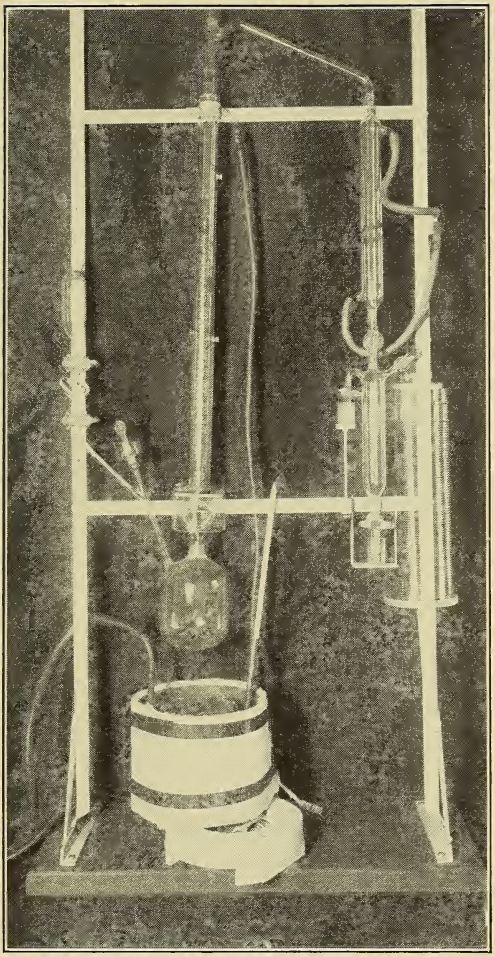

FIG. 5.—*Rectifying still for vacuum distillation*

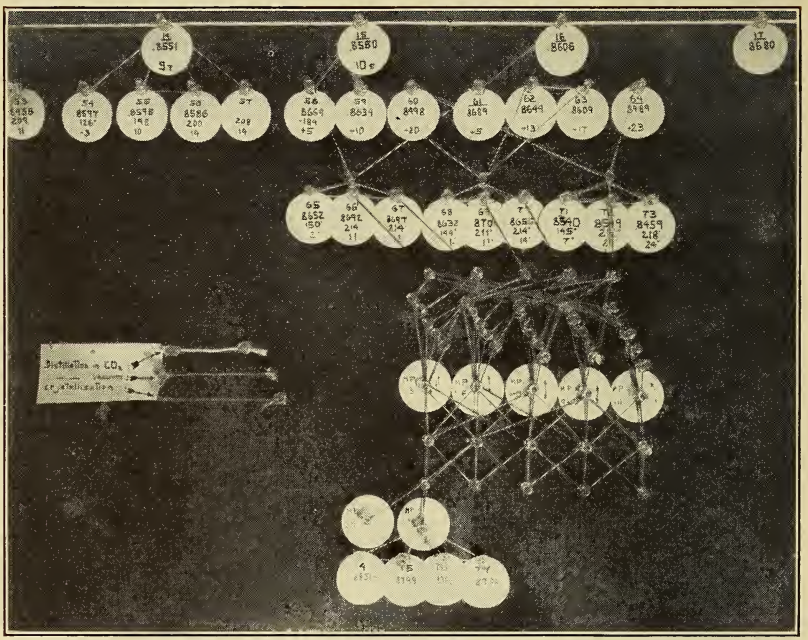

FIG. 6.—*Fractionation flow chart*

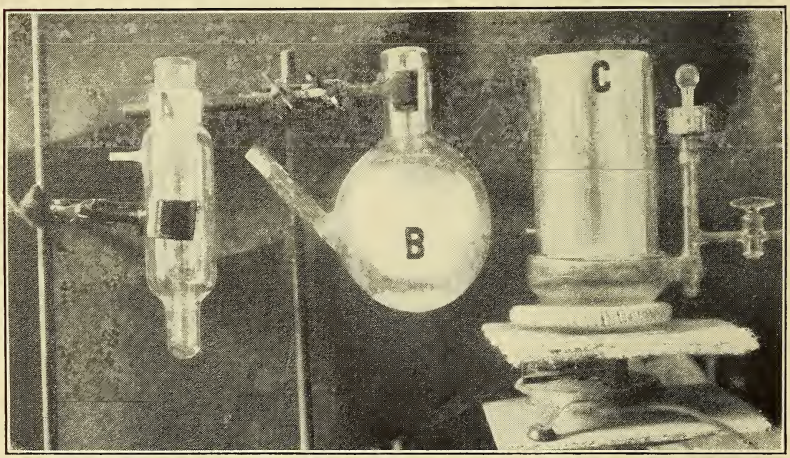

FIG. 7.—*Group of molecular stills*

because they can not be heated without decomposition, can be rather easily distilled even at room temperatures by what may be called a "molecular still," a type first used by Brönsted and Hevesy[4] for separating the isotopes of mercury.

1. THE ESSENTIAL FEATURES OF THE MOLECULAR STILL

The essential features of this type of still are the following:

1. A high vacuum. For securing this vacuum, means should be available for producing a vacuum equal to, or preferably better than, the vapor pressure of the substance at the temperature at which it is to be distilled.

2. A large and clean area of evaporating surface.

3. A short distance between the evaporating surface and the condenser.

4. A sufficient temperature difference between the distilling surface and the condensing surface.

With a still constructed according to these principles such materials as mercury, paraffin wax, and calomel, for example, can be distilled at room temperature. It is not necessary that the substance to be distilled be in the liquid state at the distilling temperature, although fractionation without the necessity of provision for artificial stirring is, of course, more rapid with liquids.

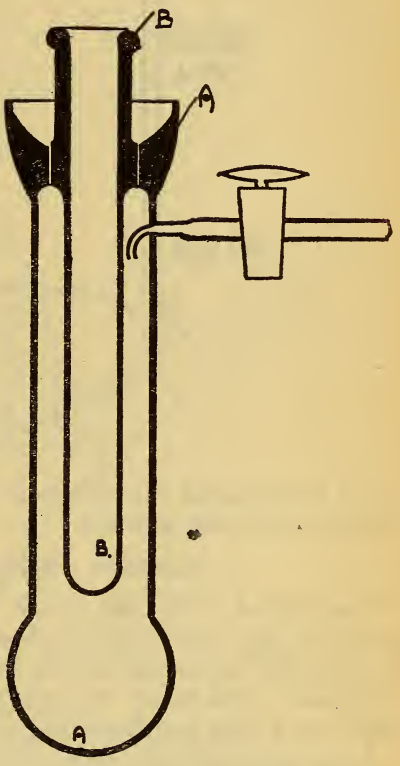

FIG. 8.—*Molecular still*

2. TYPES OF CONSTRUCTION

Various forms of molecular stills are shown in accompanying Figures 7, 8, 9, 10, and 11. In all cases the substance to be distilled is placed in the receptacle *A* and the cooling agent (for example, liquid hydrogen, liquid air, carbon dioxide snow mixed with a suitable liquid, ice and salt, etc., according to the temperature gradient required) is placed in the receptacle *B*. The forms shown in Figures 10 and 11 make it possible to distribute the substance to be distilled in a layer over the interior surface of the vessel *A*, with consequent increase in the rate of distillation. The temperature of the substance in *A* during the distillation is controlled by immersing this part of the apparatus

[4] Brönsted and Hevesy, Phil. Mag., 43, p. 31; 1922.

in a suitable bath (for example, mercury) provided with a means for regulating its temperature.

The forms shown in Figures 8 and 11 are designed to permit the easy removal of the distillate. In the case of the forms shown in Figures 9 and 10 separation may be effected (*a*) by pipetting out or dissolving out the undistilled residue, (*b*) by freezing the undistilled residue, inverting the apparatus, melting the distillate, and allowing it to flow into a position from which it can be removed by a pipette,

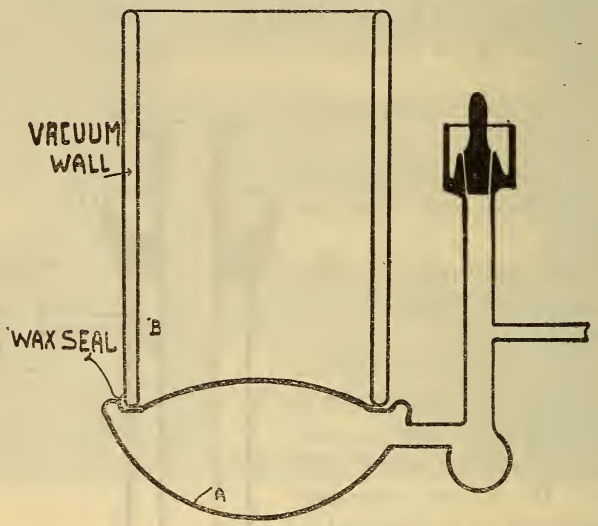

FIG. 9.—*Molecular still*

or (*c*) by breaking the apparatus. Various other forms of construction are obviously possible.

3. HISTORY OF THE MOLECULAR STILL

The rate of distillation under conditions analogous to those which prevail in this type of still has been employed by Langmuir and others as a method for measuring the vapor pressure of metals at high temperatures. The theory of the process is fully discussed in Langmuir's papers and need not therefore be repeated here.[5]

Apparently the only application of the molecular still for purposes of purification by fractional distillation is that described by Brönsted and Hevesy, who used it to separate the isotopes of mercury.[6] It should have, however, a wide range of utility as a general laboratory method, particularly for substances which can not be distilled by the customary methods on account of decomposition.

4. RATE OF DISTILLATION

Under conditions such that no recondensation occurs on the evaporating surface the rate of distillation of a given molecular

[5] See, for example, Jones, Langmuir, and Mackay, Phys. Rev., **30**, p. 201; 1927; and the literature there cited. See also Knudsen, Ann. Phys., **47**, 697; 1915.

[6] See footnote 4, p. 477.

species in a molecular still may be calculated by means of the Langmuir equation

$$n = pS\sqrt{\frac{1}{2\pi MRT}} \qquad (1)$$

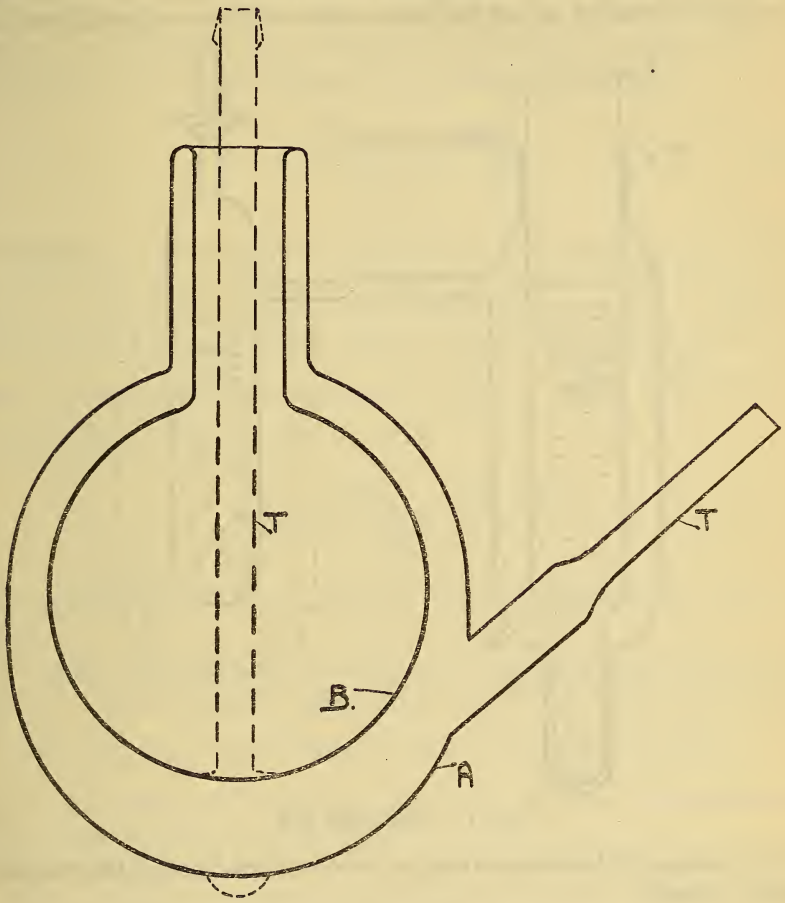

FIG. 10.—*Molecular still. Dewar-flask type*

The tube T may be placed in either of the two positions shown

in which n is the number of moles of the substance which distill in one second, p is its vapor pressure at the evaporating surface at $T°$ K., and S is the effective area. M is the molecular weight and R the gas constant. For example, if $M=400$, $p=0.001$ mm Hg, $S=10$ cm^2, and $T=300°$ K., we find

$$n = 0.001 \times 1333 \times 10\sqrt{\frac{1}{2 \times 3.14 \times 8.32 \times 10^7 \times 300 \times 400}}$$

$$= 17 \times 10^{-7} \text{mole/sec.} = 0.7 \text{ mg/sec.}$$

The actual rate of distillation will, in general, be less than the calculated value, owing to some reflection of molecules from the condensing surface, but such reflection will at worst never amount to more than 90 per cent,[7] so that the actual rate will never be less than 0.1 of the calculated rate if the temperature of the condensing surface

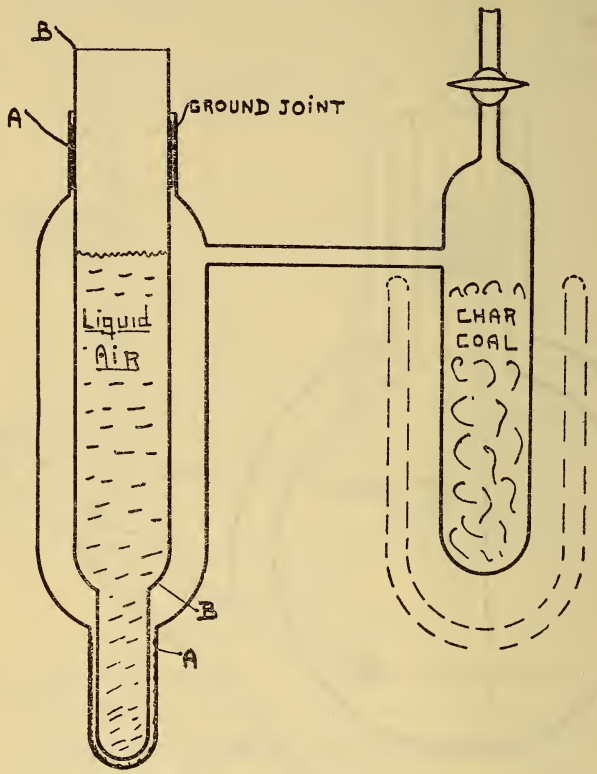

FIG. 11.—*Molecular still*

is low enough, if the evaporating surface is clean,[8] and if the vacuum is high enough.

5. SELECTION OF THE COOLING AGENT

The cooling agent may be selected from the following considerations: p_e = the vapor pressure at the temperature T (°K.) of the evaporating surface, and p_c = the desired vapor pressure at the temperature $(T-\Delta t)$ of the condenser. Let $\frac{p_e}{p_c}=x$. Then

$$\Delta t \lessdot \frac{T \log_{10} x}{\log_{10} x + \phi \frac{T_B}{T}} \text{ approx.} \qquad (2)$$

in which T_B is the normal boiling point in °K. If this is known, the constant ϕ can be obtained from International Critical Tables, vol-

[7] Langmuir, Phys. Rev., 7, p. 176; 1916; and International Critical Tables, 5, p. 53.
[8] Clean; that is, free from a layer of lower volatility. *v. infra.*

ume 3, page 246. This relation assumes that the condensate is in the form of a supercooled liquid. In many cases it will be crystalline, in which case the required Δt will be smaller than that given by the above relation.

The following example illustrates the use of relation (2): If we take $x=100$, which is large enough for any practical case, and if we put $T=300°$ K. (room temperature), relation (2) becomes

$$\Delta t < \frac{300\times 2}{2+\phi\frac{T_B}{T}} = \frac{600}{2+\phi\frac{T_B}{T}} \qquad (2a)$$

Suppose the substance to be distilled is anthraquinone, for which $T_B=653°$ K. This substance falls in Group 0 of Table 3 (I. C. T., vol. 3, p. 247) and from Figure 1 (p. 246) we find $\phi=5.0$ at $t_B=380°$ C. From figure 2 (p. 247), using benzene as the type substance, we find that ϕ increases about 0.5 unit between $\frac{T}{T_B}=1$ and $\frac{T}{T_B}=\frac{300}{653}$. Hence, substituting in equation (2a) we have

$$\Delta t < \frac{600}{2+5.5\times\frac{653}{300}} < \frac{600}{12.9} < 46°$$

The temperature of the condenser should therefore be $-19°$ C. or lower.

In many cases the normal boiling point of the substance will not be known. For such cases a safe upper limit for Δt may be computed by taking $T_B < 1.5T$, which gives (for $x=100$) $\Delta t_{max.}=\frac{2T}{2+1.5\phi}$.

For the distillation of organic compounds at room temperatures it will usually suffice to take $\Delta t < 60°$.

In this connection it should be pointed out that the ordinary type of still, in which the temperature difference between distilling surface and condensing surface is small and in which the rate of distillation is proportional to the difference between the two vapor pressures, is also capable of practical operation for distillations with vapor pressures as low as 0.05 mm., if the condenser is placed within the distillation chamber as in the apparatus described by Volmer.[9]

6. AZEOTROPIC MIXTURES

If the mixture which is being distilled is an azeotropic mixture, no separation is secured in the ordinary types of stills. In the molecular still, however, fractionation of such a mixture will, in general, result, as Brönsted and Hevesy have pointed out, because from equation

[9] Volmer, Z. angew. Chem., 34, p. 150; 1921.

(1) it is evident that the rate of evaporation of a given molecular species is determined not alone by its partial vapor pressure, but also by its molecular weight. There is, however, also a condition under which no fractionation will occur in a molecular still, namely, when the ratio $\frac{p_1}{p_2}\left(\frac{M_2}{M_1}\right)^{\frac{1}{2}}$ is equal to the molecular ratio $\frac{n_1}{n_2}$ in the liquid phase, for each of any two molecular species present. Under these conditions the condensate would have the same composition as the original liquid. For mixtures which are ideal solutions this is equivalent to the condition that the ratio $\frac{p_o}{M^{\frac{1}{2}}}$ shall be the same for all molecular species present, p_o being the vapor pressure in the pure state. Since, however, for members of the same homologous series p_o decreases as M increases, fractionation of such mixtures in a molecular still is advantageously affected by the variations in both p_o and M.

The condition that $\frac{n_1}{n_2}=\frac{p_1}{p_2}\left(\frac{M_1}{M_2}\right)^{\frac{1}{2}}$ might, however, conceivably occur quite as frequently as the condition of azeotropism in ordinary distillation. The case that any mixture will satisfy the conditions for distilling in unchanged proportions by both methods is limited to mixtures of substances of equal molecular weights and equal vapor pressures at all temperatures and will never be encountered except with mixtures of two optical isomers. Hence, practically every mixture should be subject to fractionation in either the usual still or the molecular still. It might, of course, be possible that a series of alternate fractionations by the two methods would be necessary to accomplish the most complete separation, if distillation alone is employed.

7. ILLUSTRATIVE EXPERIMENTS

A sample of paraffin wax having an initial freezing range of 54.1 to 51.7° was separated into two fractions by a single distillation at 55° C. in the still shown in Figure 9, using carbon dioxide snow as the cooling agent. The distillate had a freezing range of 48.6 to 48° and the residue a freezing range of 57.1 to 56.5°.

A sample of cane sugar was distilled at 120° C. The distillate was a white solid, sweet in taste and dextro rotatory in aqueous solution.

Another example of the use of stills of the general type shown in Figures 8 and 10 is described in connection with Brönsted and Hevesy's experiments on the isotopic separation of mercury.[10]

Since mercury is a convenient substance for testing the efficiency of a given type of molecular still with reference to the rate of dis-

[10] See footnote 4, p. 477.

tillation obtainable in practice as compared with the rate calculated from equation (1), an experiment was carried out with mercury in the still, shown in Figure 10. The lower part of the still containing the liquid mercury was immersed in a bath of mercury kept at 0° by means of an ice pack. A thermometer inserted through the side arm indicated the average temperature of the distilling surface during the distillation. Liquid air was placed in the inner chamber *B*. The following results were obtained: [11]

Time of distillation	hours	4. 0
Area of distillation surface	cm^2	48. 0
Temperature of distilling surface	°C	−0. 2
Vapor pressure at distilling surface	mm	0. 00018
Weight of distillate obtained	g	5. 2
Weight of distillate calculated	do	6. 2
Efficiency	per cent	84

The test experiments with the molecular still on mercury, paraffin wax, and calomel were carried out by Mildred M. Hicks; those with cane sugar, by Dr. R. T. Leslie and S. T. Schicktanz.

PART 6

VI. METHODS OF FRACTIONATION BY CRYSTALLIZATION OR MELTING AND OF DETERMINING FREEZING-POINT CURVES

By Mildred M. Hicks

In addition to its value as a primary method, fractionation by crystallization or fusion is convenient for breaking up azeotropic mixtures. The fractionation may be carried out either with or without the use of a solvent. For the higher petroleum fractions, such as lubricating oil, petrolatum, or wax, the use of a solvent is usually desirable.

The following solvents have been studied in this connection: Methyl alcohol, glycerol, ethyl ether, acetone, chloroform, carbon

[11] *Note on poison hazards from spilled mercury.*—In recent literature attention has been directed to the dangers of mercury poisoning in rooms containing exposed mercury surfaces resulting from spilled mercury lodged in floor cracks and other crevices from which its removal is difficult. The vapor pressure of pure mercury at room temperatures is of the order 0.001 to 0.003 mm Hg, and if the air of the room were only partially saturated with this mercury vapor, continued exposure thereto might constitute a hazard. One experiment on the rate of distillation of mercury carried out as described above apparently throws some light upon the question.

In this experiment the distillation was carried out for seven hours. Instead, however, of obtaining approximately the theoretical yield of 9 g of distillate, no distillate whatever was obtained. Examination of the mercury surface showed that it was contaminated with a barely visible layer of stopcock grease which was apparently sufficient to completely stop appreciable vaporization in this period of time. It seems probable, therefore, that the hazard from spilled mercury in a laboratory soon disappears by the natural contamination of the mercury surface in a short period of time. In any case a spray of heavy oil on the surface of spilled mercury would appear to be an adequate means of eliminating all hazard in ventilated rooms.

This is also the conclusion reached by Gaede (Ber. Naturforsch. Ges. Freiberg i. Br., **18**, p. 174; 1911), who found that the vapor pressure of Hg at room temperature, as registered in his manometer, fell from 0.0013 mm to zero after admitting air from the room (apparently through a stopcock) and again reevacuating, and then slowly rose to only 0.00007 mm after several hours.

tetrachloride, carbon disulphide, acetic acid, benzene, toluene, petroleum ether, and kerosene. Of these, ethyl ether was found to be one of the best, and it has been the principal one employed thus far. The fractionation may be carried out by any one or more of the following procedures:

1. By cooling the solution.
2. By evaporating the solvent at any controlled temperature.
3. By precipitation with a second solvent.
4. By complete solidification of the solution, followed by equilibrium melting.

FIG. 13.—*Apparatus for determining time-temperature cooling curves*

All of these procedures have been used, but the fourth one [12] has proved most convenient for most of the work up to the present. In this procedure the solidified solution is placed on a porous support in a vacuum-jacketed funnel fitted with a thermometer and stirrer. The melting mass is stirred so as to maintain equilibrium, and the liquid fractions which drain through are removed from time to time in accordance with the thermometer readings. Some forms of vacuum funnels employed for this purpose are shown in Figure 12.

The time-temperature cooling curve is a convenient index of the progress of the fractionation. For obtaining this curve the apparatus shown in Figure 13 is employed. Some typical curves obtained in this way are shown in Figures 14, 15, and 16. The values in the F. P. column are the initial freezing points.

It may be stated at this point that in the present investigation there has been found no petroleum fraction which can not be completely and readily obtained in crystalline form. Fractionation by crystallization is therefore possible at any stage of the work except possibly in the case of tarry or asphaltic materials. These have not been studied.

[12] See also Timmermans and Martin, J. chim. phys., 23, p. 6; 1926.

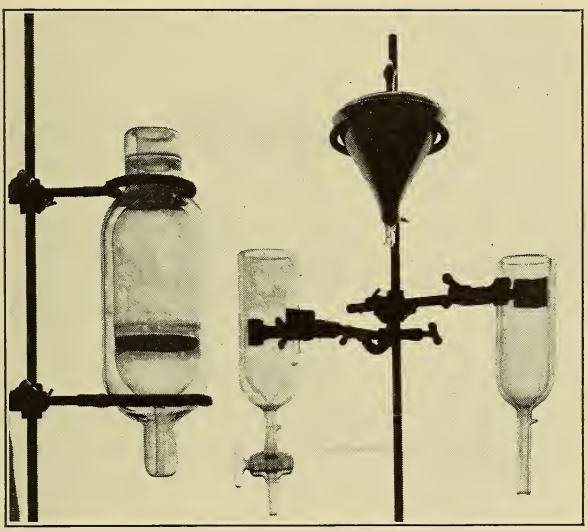

FIG. 12.—*Types of vacuum funnels*

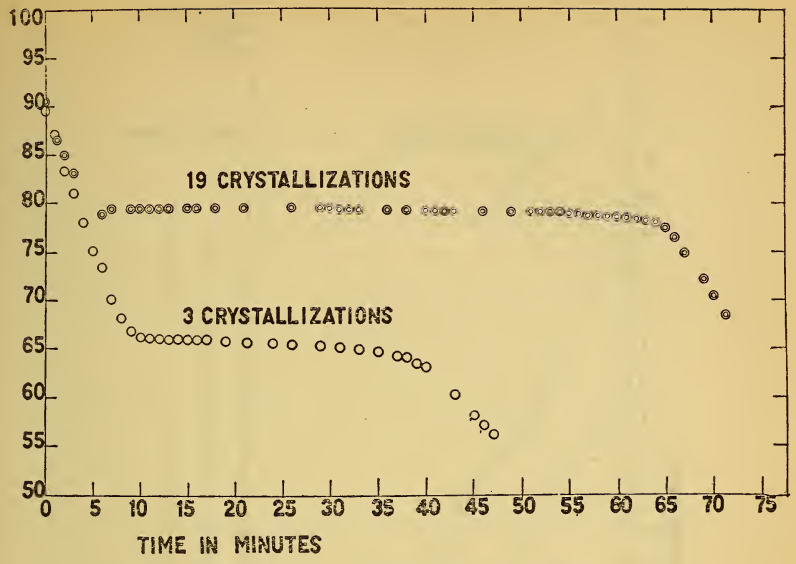

FIG. 14.—*Typical cooling curves*

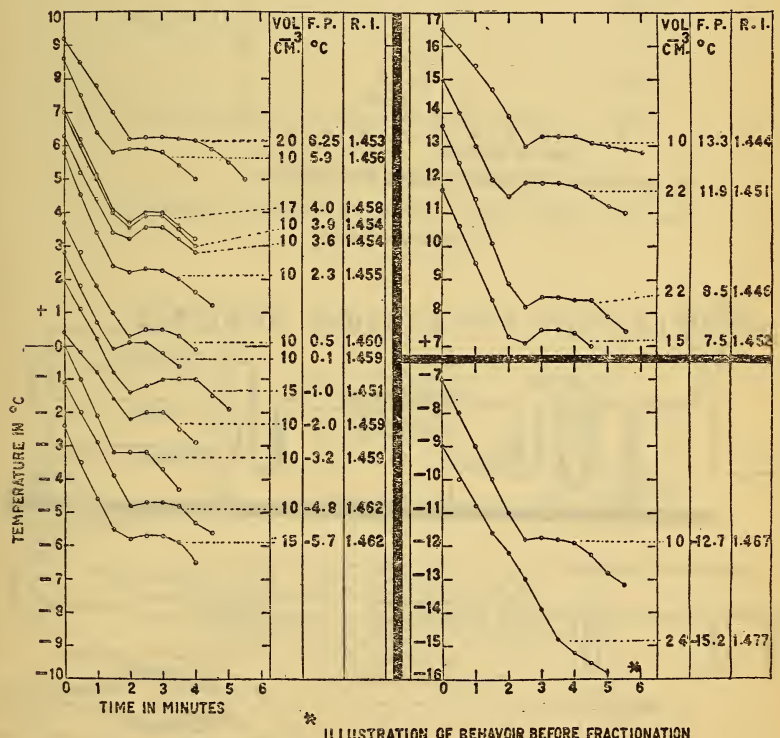

FIG. 15.—*Cooling curves of gas-oil fractions after extensive fractionation by both distillation and crystallization*

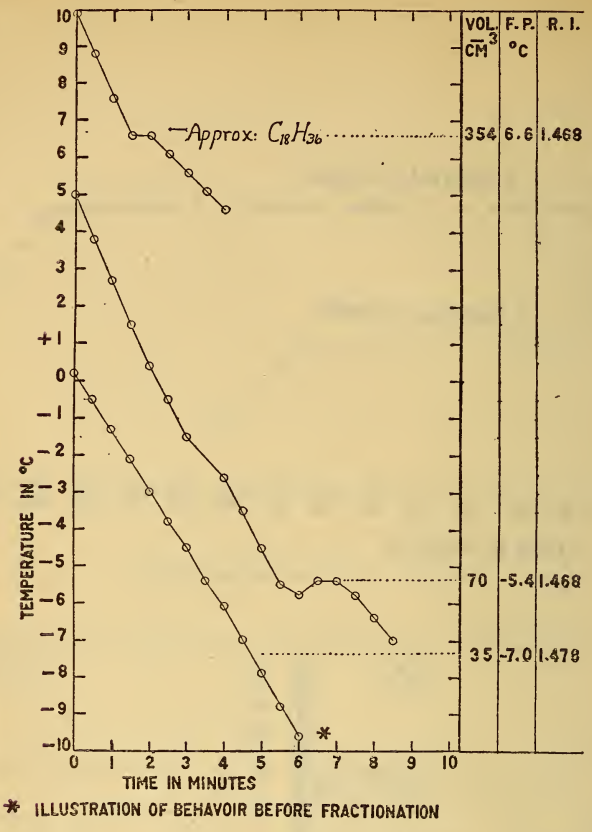

FIG. 16.—*Some cooling curves of fractions subjected to distillation only*

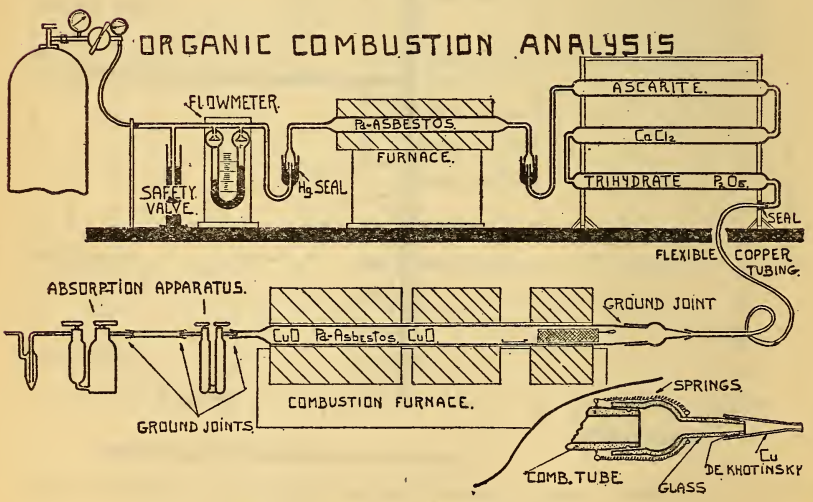

FIG. 18.—*Apparatus for combustion analysis. Detail*

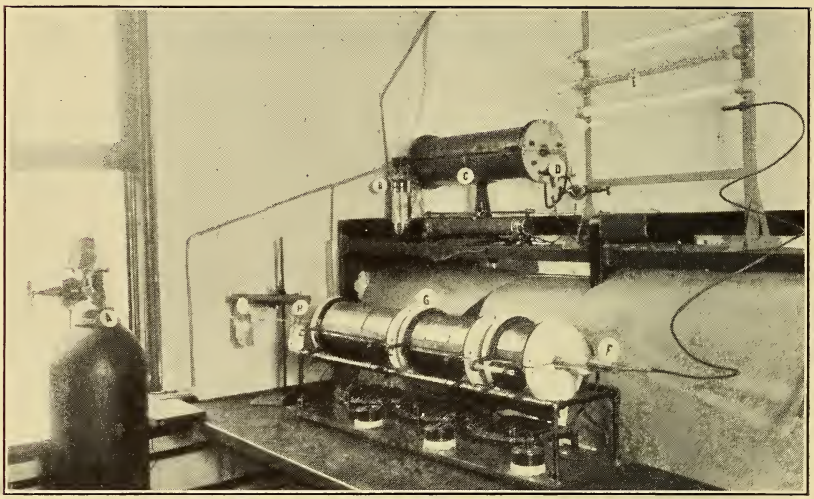

FIG. 17.—*Apparatus for combustion analyses*

A, oxygen tank
B, flow meter
C, furnace for the destruction of organic impurities. Contains a glass tube filled with palladized asbestos
D, mercury seal joint (one on each side of the furnace)
E, purification train filled with $CaCl_2$, ascarite, magnesium perchlorate trihydrate, and P_2O_5. This train, by means of flexible copper tubing is connected to: *F*, ground-glass nonlubricated joint; *G*, the combustion furnace; *H* and *I*, water and CO_2 absorption bulbs (all connections are ground glass-to-glass joints)

PART 7

VII. APPARATUS FOR COMBUSTION ANALYSIS

By Johannes H. Bruun

The combustion apparatus is illustrated in Figures 17 and 18. The only features not usually found in such apparatus are (1) the provisions for insuring the required purity of the oxygen and (2) the use of wax-sealed metal-to-glass or of glass-to-glass joints only, throughout the combustion train.[13] The following results obtained with the apparatus indicate the accuracy with which combustion analyses can be duplicated. With this degree of accuracy in the combustion analysis it is possible, with the aid, when necessary, of a molecular weight determination, to determine with certainty the empirical formula of any hydrocarbon up to C_{100}.

TABLE 5

COMBUSTION OF RESUBLIMED NAPHTHALENE (NOT PURE)

Run	H	Deviation	C	Deviation	Sum
	Per cent		*Per cent*		*Per cent*
1	6.27	0.02	93.61	0.02	99.88
2	6.21	.04	93.66	.03	99.87
3	6.26	.01	93.61	.02	99.87
Average	6.25	.023	93.63	.023	99.87
Theoretical	6.29		93.71		100.00

COMBUSTION OF A GAS-OIL FRACTION (LIQUID)

1	13.66	0.02	86.10	0.03	99.76
2	13.64	.00	86.05	.02	99.69
3	13.61	.03	86.08	.01	99.69
Average	13.64	.017	86.07	.02	99.71

PART 8

VIII. SUMMARY

This paper contains a description of apparatus and methods devised and employed for the fractionation of petroleum into its constituent hydrocarbons. They include the following:

1. A rectifying still with a 20-plate column and with means for independently controlling and measuring the temperatures of the plates. The still is designed for distillation in a stream of an inert gas (CO_2) with or without boiling. It is provided with a purifying train for the CO_2, with a series of condensers with stepped temperatures down to $-80°$ C., and with a final absorber for the CO_2.

[13] For quantitative data relative to the magnitudes of the errors arising from the presence of (*a*) rubber connections, (*b*) stopcock lubricants, and (*c*) impurities in the oxygen, see Lindner (Ber. 60 B: p. 124; 1927) and the literature there cited.

2. A set of all-glass rectifying stills for vacuum distillation. These stills have vacuum or air jacketed columns, mercury-sealed stopcocks, and provision for intermittent feeding of liquid and withdrawal of fractions during the distillation. They are heated by immersion in an electrically heated bath of nickel shot.

3. Various types of molecular stills by means of which distillation can be carried out at any temperature at which the vapor pressure at the distilling surface is not lower than, say, 10^{-6} mm Hg.

4. Methods and apparatus for fractionation by crystallization or melting.

5. An apparatus for combustion analysis, with special provisions for purifying the oxygen employed, and with all rubber connections eliminated. With this apparatus the combustion analysis of a hydrocarbon can be duplicated with the following average precision: Per cent C and H each to about ± 0.05. This makes it possible to determine with certainty the values of n and x in the formula C_nH_{2n+x}, for any hydrocarbon up to C_{100}.

The change in the iodine number of the "wax-distillate" fraction of a petroleum oil produced by heating it for different periods and at different temperatures up to 370° C. in (*a*) air and (*b*) H_2, N_2, and CO_2, respectively, has been determined, and it is shown that in the absence of air the rate of this change is greatly reduced, thus making it possible to distil petroleum at high temperatures without cracking, provided all air is excluded.

Evidence is presented showing that the hazards from exposed mercury surfaces in a laboratory are eliminated as soon as the mercury surface becomes contaminated with a continuous layer of a heavy oil or grease.

ACKNOWLEDGMENT

This paper describes the apparatus and methods which have been developed and are being employed in an investigation on "The separation, identification, and determination of the chemical constituents of commercial petroleum fractions" listed as Project No. 6 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the institute with the cooperation of the Central Petroleum Committee of the National Research Council.

WASHINGTON, August 4, 1928.