U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1372

*Part of Journal of Research of the National Bureau of Standards, Volume 26, March 1941*

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# ANALYTICAL SEPARATION AND PURIFICATION OF GASES BY FRACTIONAL DISTILLATION AND RECTIFICATION AT LOW TEMPERATURES

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## ABSTRACT

**This paper describes the apparatus and general procedures used at this Bureau for the separation of gases by distillation and rectification at low temperatures. The subject is treated from two viewpoints—analytical separation, and the preparation of pure gases.**

## CONTENTS

## I. INTRODUCTION

The gas analyst has at his disposal a number of attractive physical methods which may be invoked in time of need to supplement or even replace the various chemical methods at his command. By far the most useful of these is distillation. Unlike most of the other physical methods, distillation can achieve the actual separation and isolation of the various components of a complex mixture. It can accordingly be used for both analysis and purification of gases, and is not limited (as are many physical methods) to binary mixtures. Although distillation has been used industrially for many years, its application to gas mixtures in the laboratory is relatively recent, most of the development having taken place during the last 20 years. This development in our country is attributable to the demand of the natural gas and associated industries, and arose from the necessity of knowing, insofar as possible, the actual composition of complex mixtures of hydrocarbons—an analysis that could not be made by the time-honored method of combustion. Methods of distillation have since been applied to various gaseous mixtures, and have recently been used by many industrial research laboratories.

Despite this, the distillation of gases has not been subjected to anything like the standardization accorded the ordinary chemical methods, and has been given mention by title only, if at all, in standard texts on gas analysis. This situation is understandable and will probably be remedied during the course of time.

The method of distillation as applied to gases has one fundamental and several practical limitations. Azeotropic mixtures cannot be separated by this means, and often the separation of components of like boiling points is so exacting and irksome that one had better look elsewhere for help if it is available. It is often advantageous to supplement distillation with methods capable of dealing with binary mixtures yielded as distillates. Again, the apparatus involved is of necessity relatively complicated and expensive. The chief objection from the industrial viewpoint is the time required for an analysis. Our experience agrees with that of a great many others, and clearly indicates the necessity for separation on a fractional pattern in many instances, rather than performing a single straight distillation. This increases the time required to an extent considerably greater than is implied by some papers on the subject.

This paper describes the apparatus and general procedures used at this Bureau for the separation of gases by this method. The separation of natural gases by isothermal fractional distillation has been previously described.[1] The present apparatus retains the essential features of the old one, although in greatly simplified form. In addition, special rectifiers for handling large samples have been included. The new apparatus was designed primarily for the preparation of pure gases to be used for determinations of the accuracy (and reproducibility) of methods of gas analysis, but as such it is an equally effective analytical tool. If purification of gases were the sole instead of the main object, some parts of the apparatus could be dispensed with. If the reverse were true, other portions of the apparatus could be eliminated. In the description which follows, the purposes will be distinguished so that a prospective user can easily determine what may be needed for his own work.

## II. APPARATUS

### 1. GENERAL ASSEMBLY

The best introduction to the apparatus is offered by the series of photographs which follow.

Figure 1 shows the complete assembly viewed from the right. It is one continuous piece of glass from end to end, with no rubber connections. The various glass parts are mounted on an iron frame and fused together. The glassblowing was done by E. O. Sperling, Chief Glassblower of this Bureau, and has been generally considered by technical visitors to be one of the finest examples of this art. Each of the five prominent aluminum spheres at the top encloses a 22-liter Pyrex flask embedded in roller composition.[2] Once used as

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[1] Martin Shepherd, BS J. Research 2, 1145 (1929) RP75.

[2] This is glycerol and glue. Ground cork was added to this. The mixture sets to a rubber-like mass resembling fruit cake, and affords excellent protection and some thermal insulation to the flasks.

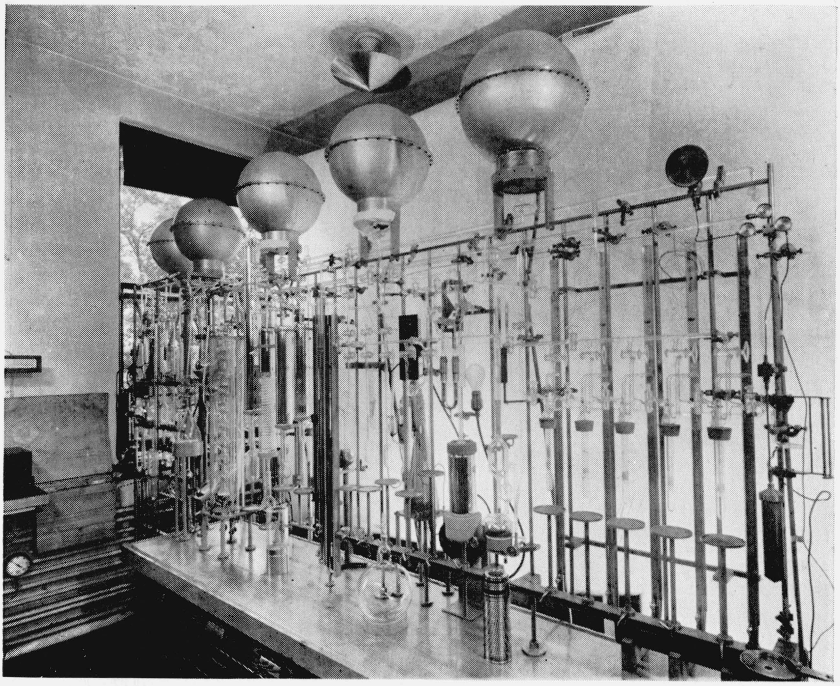

FIGURE 1.—*Complete apparatus viewed from the right end.*

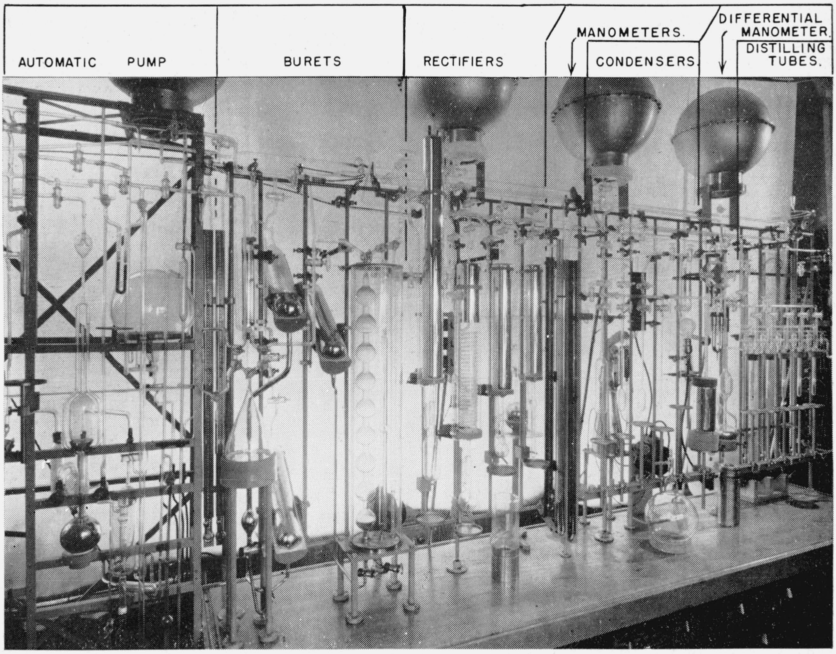

FIGURE 2.—*Apparatus from the left end, showing major sections.*

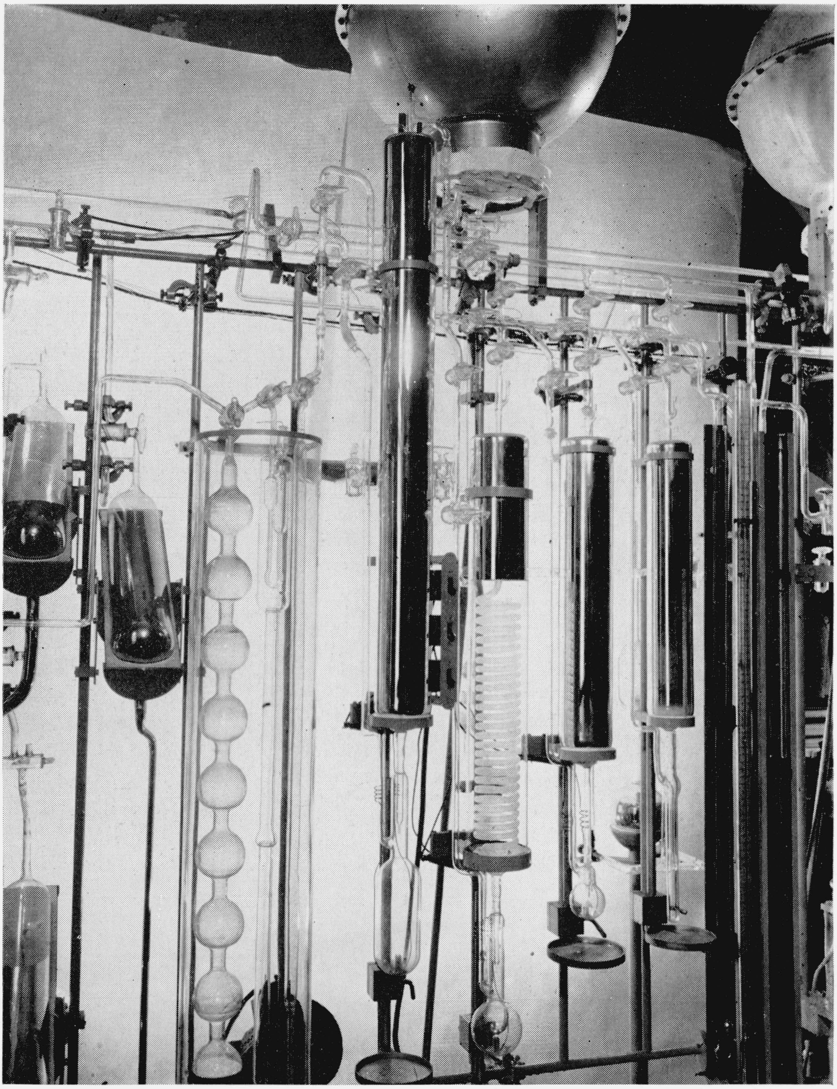

FIGURE 3.—*Detail of burets, rectifiers, and manometers.*

stratosphere samplers, they now serve as reservoirs for the storage of gases.

Figure 2 shows (almost completely) the apparatus from the left. This photograph has been marked to show the various major sections that comprise the whole apparatus. From left to right, these are:

(1) An automatic sample-collecting pump, which has been previously described in detail.[3] This is a mercury-displacement pump that is used to collect noncondensible gases. Since it acts as the backing pump for a mercury-vapor pump, its action is fairly rapid by comparison with the usual pumps of this type. It is, however, rarely used except for special problems sometimes associated with the analysis of small samples.

(2) The next section is for volume measurement. A calibrated bulb of 1-liter capacity, a bulbed buret of 1-liter capacity, and a standard 100-ml burette are connected to permit the common use of a manometer-compensator unit. Placed between the 1-liter bulb and the bulbed burette are three inclined reservoirs which supply mercury to these units.

(3) The next section has four rectifying columns of different sizes. The first two are designed primarily for the preparation of pure gases. The second pair is for the analytical separation of gas mixtures, and serves for samples of large or small volume.

(4) Following the rectifying section are three manometers for registering pressures in the rectifiers and receivers.

(5) Next is a series of five condensers to receive liquid distillates from the columns.

(6) Then comes an important part of the apparatus—the differential saturation-pressure manometer by means of which the purity of distillates is determined.

(7) Following this is a series of distilling tubes for the analytical separation of small samples by isothermal distillation.

(8) The final section, not shown in this figure but apparent at the extreme right end of figure 1 (and shown also in figures to follow), is a unit for the transfer of gases from the glass apparatus to cylinders where they may be stored at high pressures.

These are the essential units that make up the apparatus. They may now be considered in more detail.

## 2. GAS MEASURING AND RECTIFYING SECTION

Figure 3 shows the rectifiers, with the bulbed burette at the left and manometers at the right. The burette and manometer-compensator have been previously described.[4] The system permits measurement of gas volumes up to 2 liters at the fixed pressure of the compensator (approximately atmospheric). The measuring unit is connected to the inlet of the rectifiers, and mercury from the burette is prevented from accidentally entering the rectifiers by a spherical float valve interposed in the line.

The rectifying columns are connected to permit the following procedures:

1. The distillate can be discharged into evacuated receivers at controlled rates, and the distilling pressure and receiver pressure measured independently.

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[3] E. R. Weaver and Martin Shepherd, J. Am. Chem. Soc. **50**, 1829 (1928).

[4] Martin Shepherd, BS J. Research **6**, 125-127 and 140, figures 4 and 13 (1931) RP266.

2. The distillate can be discharged into condensers and collected as a liquid.
3. Any column can be isolated and used alone.
4. The columns can be connected in series, so that one acts as a receiver for another.
5. The columns can be connected in parallel, so that several can discharge simultaneously into a common receiver.
6. One or more columns can discharge into evacuated receivers while others, operating on a different mixture, may discharge simultaneously into the condensers.
7. Distillates from one column can be taken into a column either to the right or left.
8. Distillates from either group of receivers can be taken back into any column.
9. Condensates or gases from any part of the apparatus to the right of the rectifier section can be returned to this section.

The manometers are connected so that the distilling pressures can be measured when the distillates are discharged to the condensers as well as when they are discharged to the evacuated receivers. An open-end manometer registers the distilling pressure. It is provided with an adjustable electric contact, which, when fixed at the desired pressure for distillation, flashes a light at the potentiometer when this pressure is reached. This permits the operator who has been following the temperature of distillation to make his observation at the exact moment the correct isobaric condition is reached. The other manometers are closed-end instruments of somewhat greater than barometric length, and are equipped with steel tapes that permit rapid reading. The tapes are installed as belts operating on pulleys, and two sliding collars bearing crosshairs complete the arrangement. The tape is fastened to the lower collar so that its crosshair corresponds with zero of the tape. The rectifying columns are of the spiral type illustrated in the drawing (fig. 4). This type will be recognized as an old friend, since it has been described in various modifications during the past 20 years. Evidently its real age has not been generally realized, for all of the modifications described since 1920 were cunningly plagiarized in 1895 and 1908, by Berlomont, Lebal, and Foucar,[5] who were apparently endowed with surprisingly detailed prophetic powers. The evident advantage of this type of column lies in the fact that the paths of the ascending vapor and refluxing liquid are *equal*, and, of course, of considerable length relative to the over-all length of the whole apparatus. Thus an equilibrium can be attained which is not realized if the path of the vapor is shortened with respect to that of the refluxing liquid. The column is provided with a convenient drop counter, and the boiling pot is equipped with a heater and the standard device which anyone who has used a coffee percolator will recognize. The heater is wound with platinum wire, the lead wires are very heavy, and the circuit is protected by a 3-ampere fuse. Current is regulated by means of an autotransformer.

The inner bore of the spiral is approximately 5 to 6 mm, except for the smallest column, in which it is reduced to 4 mm. Smaller bores tend to flood. In the first and third rectifier, the inside wall of the

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[5] G. Berlomont and Lebal, Bull. Soc. Chim. **13**, 674, III (1895); J. Soc. Chem. Ind. **14**, 821 (1895); Foucar, Eng. Patent 19,999 (1908).

spiral is coated with 40-mesh carborundum [6] fused to the glass. The wall is roughly etched in the second and fourth. The spiral in the first column is 6 m long; the others are 4, 3, and 2 m. The third column, with a 3-m spiral, is the only one of the group which has had the distinction of a formal test for efficiency. While the column itself is scarcely 40 cm high, it has the efficiency of 30 theoretical plates.

Temperatures in the condensers of the columns are measured by means of No. 36 copper-constantan thermocouples in connection with a precision potentiometer. Copper balls are placed in the evacuated jacket of the condenser and surround the condenser tube snugly. The heat capacity of the large amount of metal serves fairly well to maintain desired temperatures when the cooling liquid is discharged at appropriate intervals by means of a pressure seal affixed to the Dewar flask containing it. Liquid air is ordinarily used for the refrigerant.

A D'Arsonval tube (unsilvered Dewar) is placed around the boiling pot and snugly up to the bottom of the vacuum jacket of the column during its operation.

If the condenser temperature becomes too low and the distillation is interrupted, distillate can collect and freeze at the top of the column. This may happen only rarely, but if it does, pressure will build up in the column and eventually something must let go.[7] For this reason, a safety seal is teed into the column inlet. This seal has a column of mercury which retains pressures up to 2 atmospheres, but permits the escape of gas in excess of this pressure.

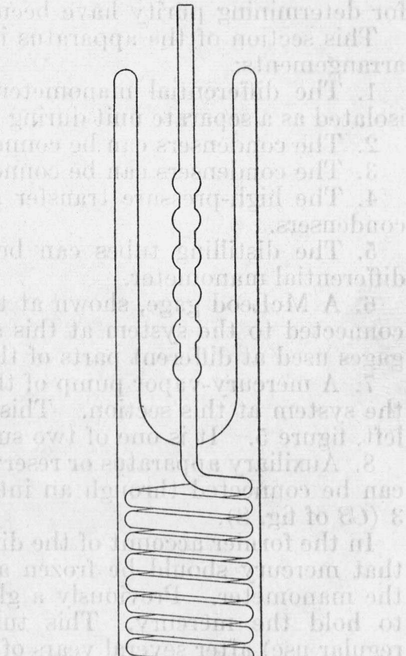

FIGURE 4.—*Drawing of rectifier.*

### 3. CONDENSERS AND DIFFERENTIAL MANOMETER

Figure 5 shows the condensers and the differential saturation-pressure manometer. The condensers are merely calibrated tubes and

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[6] This was suggested by T. Midgley, Jr. (U. S. Patent 1,961,774), who used an organic cement to secure the carborundum to the glass. Such a cement is objectionable, but the carborundum may be fused directly into Pyrex glass.

[7] In the only case on record in our laboratory, the something which let go was a slug of frozen methane, and the next thing was the mercury from the open-end manometer. This hit the ceiling with such force that it was distributed in fine globules completely throughout the room. It took two men 4 days to clean up.

hold different amounts of liquid (200 ml to 0.5 ml). The smaller ones are used in connection with the differential manometer in determining the purity of distillates. The manometer and the procedure for determining purity have been previously reported.[8]

This section of the apparatus is connected to permit the following arrangements:

1. The differential manometer and necessary condensers can be isolated as a separate unit during tests for purity.
2. The condensers can be connected back to the rectifiers.
3. The condensers can be connected to the evacuated receivers.
4. The high-pressure transfer apparatus can be connected to the condensers.
5. The distilling tubes can be connected to the condensers and differential manometer.
6. A McLeod gage, shown at the extreme right of figure 5, can be connected to the system at this section. (This is one of three such gages used at different parts of the apparatus.)
7. A mercury-vapor pump of the Stimson type can be connected to the system at this section. This can be seen back of third rod from left, figure 5. It is one of two such pumps used.
8. Auxiliary apparatus or reservoirs for delivering or receiving gases can be connected through an interchangeable joint above condenser 3 (*C3* of fig. 8).

In the former account of the differential manometer it was specified that mercury should be frozen around the two condensing bulbs of the manometer. Previously a glass tube had been successfully used to hold the mercury. This tube was eventually broken (not in regular use) after several years of service, and replacements thereafter showed a tendency to break when the mercury was frozen during the test procedure. Accordingly, a steel tube was substituted, but this caused erratic behavior of the manometer, evidently because of the conduction of heat down the walls of the steel vessel. To remedy this difficulty, a steel container was made with a large well at the bottom for the mercury and with a narrow neck leading to the top of the Dewar tube which contains the cooling medium. Radiating fins were fixed to the narrow neck of this steel container. The condensing bulbs of the manometer were enlarged to 6 mm inside diameter, so that slightly different amounts of initial distillate and final residue would result in no great difference in level of the menisci of these two condensates within the bulbs. Under these conditions, the manometer again gave a good account of itself. It is recommended that those who use the instrument study the particular one they must deal with by condensing the same gas in varying amounts into the two bulbs, in order to determine how closely the two condensates, whose saturation pressures are to be compared, must be measured before introduction into the manometer. In addition, the permissible minimum amount of condensate can be determined for each gas to be tested. This will, of course, vary not only with the gas tested, but also with the volume of the particular manometer. Measurements like these will preclude the possibliity of inadvertently setting up such conditions as a superheated gas on one side of the manometer and a saturated gas on the other. The desired information for proper operation is easily obtained, since the equipment permits measurement of a con-

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[8] Martin Shepherd, BS J. Research **12**, 184 (1934) RP643.

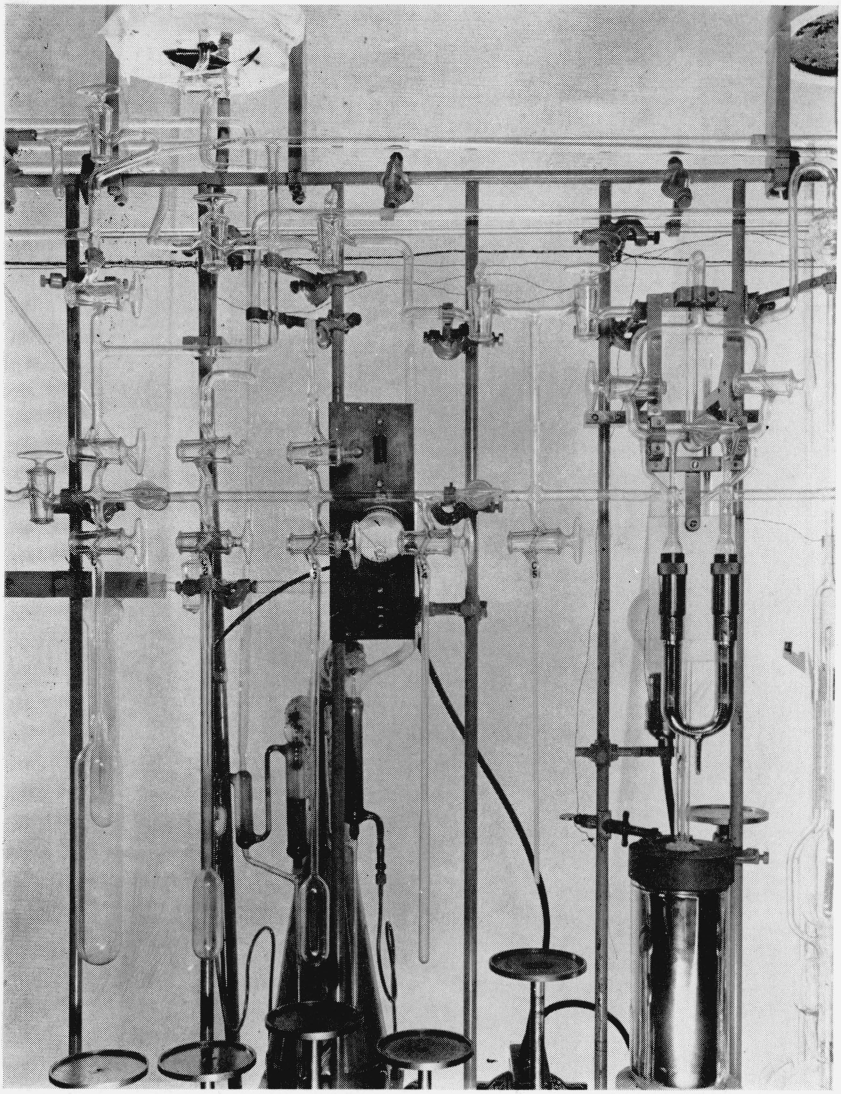

FIGURE 5.—*Detail of condensers and differential manometer.*

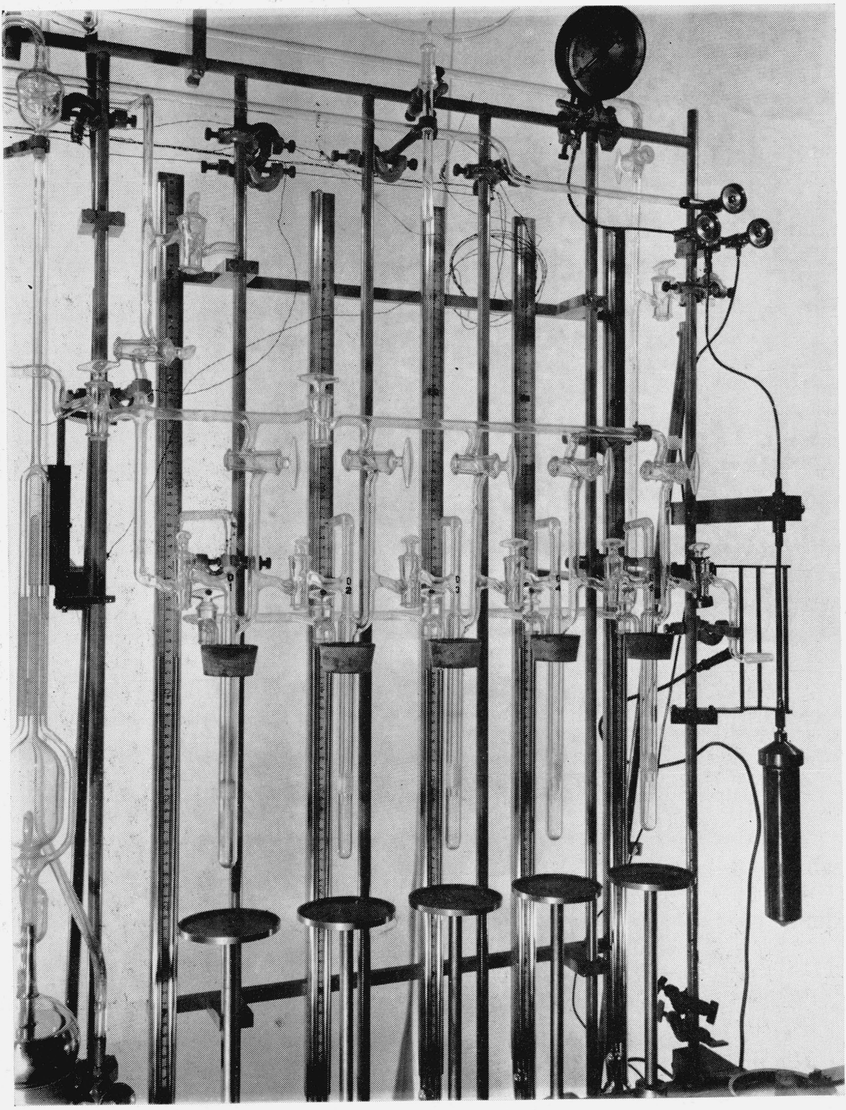

FIGURE 6.—*Detail of distilling tubes and high-pressure transfer unit.*

densate, transfer to the manometer, transfer back for a second measurement, and so on.

The manometer has proved to be an extremely sensitive instrument, capable of detecting very small traces of impurities.

## 4. DISTILLING SECTION AND HIGH-PRESSURE TRANSFER UNIT

The distilling section of the apparatus is shown in figure 6. There are five distilling tubes (*D1* to *D5*), each connected to a barometric manometer. These have been described and procedures for their use given in considerable detail.[9] The present tubes are somewhat simplified by the removal of the inner thermocouple, a feature that proved to be more of a luxury than a necessity. The unit previously described is further modified by a system of overhead connections that permits alteration of the fractionating pattern formerly reported, if this seems desirable.

The high-pressure transfer unit is the device shown at the extreme right of the apparatus. It is connected to the glass apparatus at the three needle valves (upper right) by means of a glass-to-metal joint. These valves are of the Stimson type and can be depended upon to withstand high vacuum. Gases from the apparatus can be condensed in the brass cylinder (lower right), and the whole transfer unit then isolated from the glass apparatus by means of one of the needle valves. The connections of the transfer apparatus are made of small copper tubing with silver-soldered joints. The entire metal portion of this unit is tested to 10,000 lb/in$^2$. Condensate in the brass cylinder is allowed to vaporize slowly into an evacuated cylinder, also fitted with the Stimson type needle valve. During this procedure, the pressure within the system is registered on the Bourdon gage (upper right). Gases can thus be collected and stored at high pressures without contamination.

The connections are so arranged that:

1. The distilling section can be opened directly to the differential manometer, and thence to the condenser section, evacuated receivers, high-vacuum pumps, etc.
2. The distilling section can be connected directly to the gas-measuring section, and thence to the rectifiers, etc.
3. The distilling section terminates in an interchangeable joint which permits connection to auxiliary apparatus or storage reservoirs.
4. The high-pressure transfer unit connects directly to the condenser section, and thence to other sections and the vacuum pumps.

## 5. DETAIL OF CONNECTIONS FOR BURETTES, RECTIFIERS, MANOMETERS, CONDENSERS, RECEIVERS, DIFFERENTIAL MANOMETER, DISTILLING TUBES, AND HIGH-PRESSURE TRANSFER UNIT

Figures 7 and 8 show in detail the most important connections between the various separate units of the apparatus. The line drawing (fig. 8) was made by inking directly over the photograph (fig. 7) and then removing the emulsion with a cyanide solution, thus leaving the inked flow diagram, which is accordingly a definite to-scale key of the photograph. The flow diagram shows only the most important connections on the high-vacuum side of the apparatus. Auxiliary lines on the low-vacuum side, by means of which mercury

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[9] Martin Shepherd, BS J. Research 2, 1145 (1929) RP75.

is raised and lowered in reservoirs, etc., are not shown in figure 8, since the actual arrangement of these connections must be obvious and their location is relatively unimportant. These auxiliary connections will be discussed separately. The connections of the automatic sampling pump are not shown, although the important connections to the inlet and outlet of this pump are indicated in figure 8.

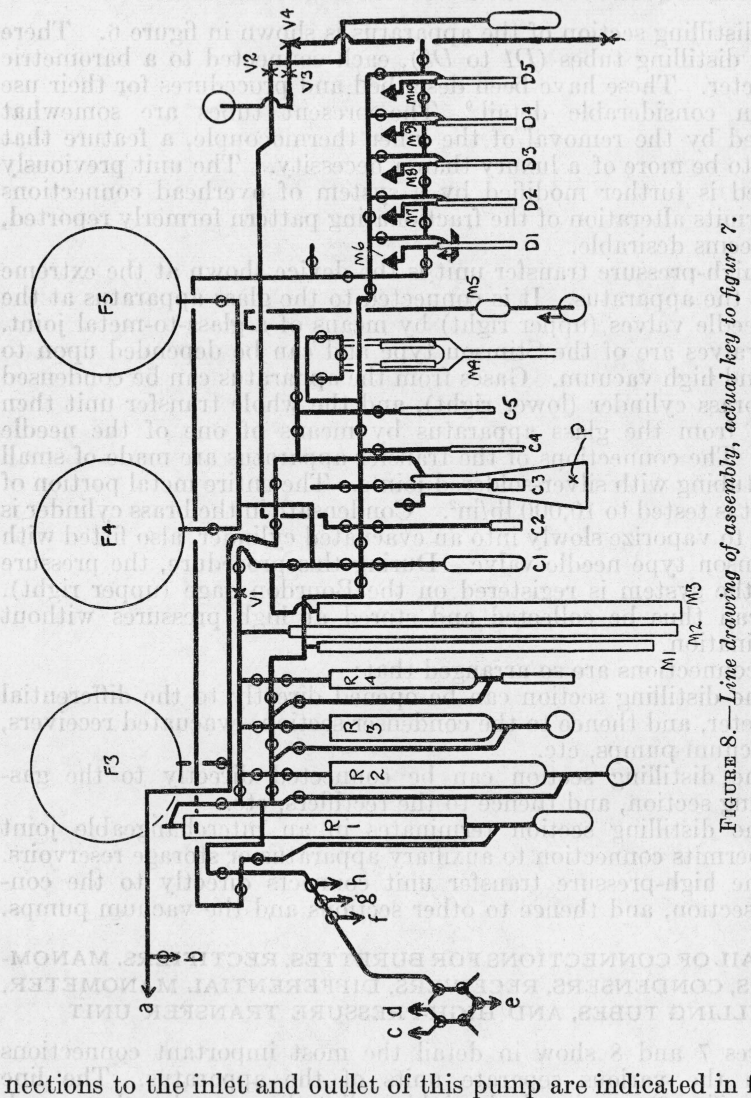

FIGURE 8.—*Line drawing of assembly, actual key to figure 7.*

Stopcocks indicated by small circles. Connecting tubes indicated by heavy lines. *C*, condensers; *D*, distilling tubes; *F*, storage flasks or receivers; *M*, manometers; *P*, pumps; *V*, valves.

*a*, to *F1* and *F2*; *b*, to inlet of automatic topler pump; *c*, topler outlet; *d*, topler inlet; *e*, 1,000 milliliter bulb; *f*, 1,000 milliliter bulbed burette; *g*, compensator, manometer unit; *h*, 100 milliliter burette.

A careful study of these two figures will reveal the actual traffic control possible. The various combinations available, which have already been enumerated in the previous discussion of the separate sections of the apparatus, will become easily apparent. Enough information is given to permit a reasonable reproduction of this portion of the apparatus.

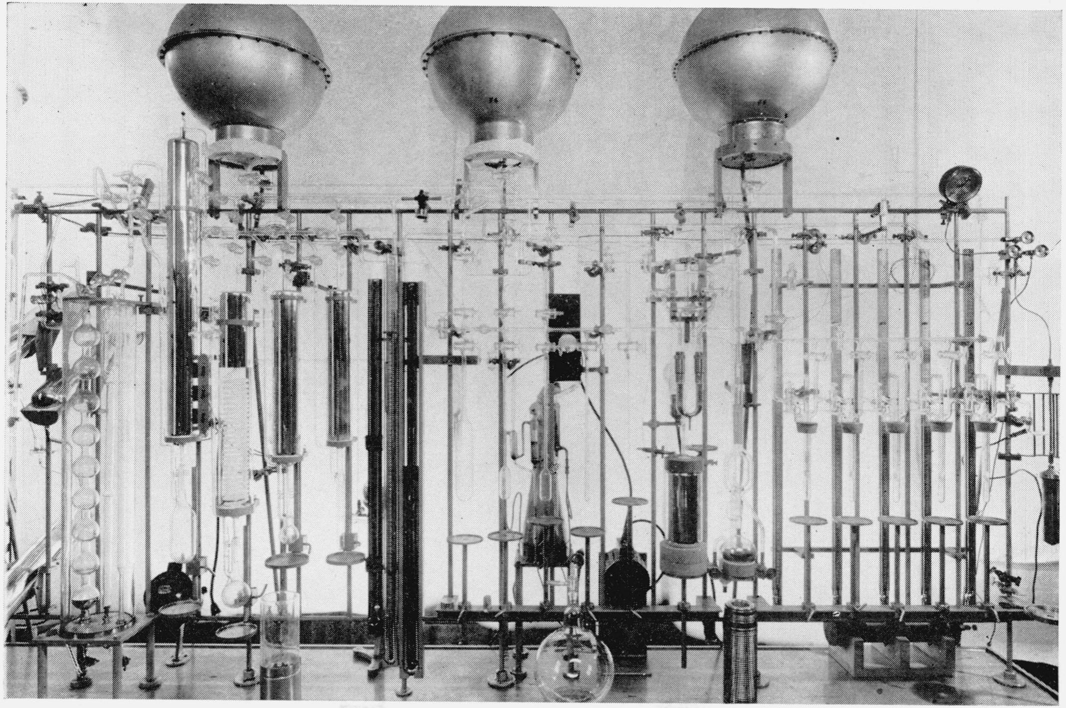

FIGURE 7.—*Detail of assembly of burets, rectifiers, condensers, differential manometer, distilling tubes, and high-pressure transfer unit.*

One feature of construction is important and should be noted. All the stopcocks used in this and other parts of the apparatus which are subjected to relatively high vacuum are simple oblique-bore cocks. No so-called "three-way", T, 120°, or other multiple-lead cocks are employed. Our experience has been that the simple cock when properly made and lubricated can be trusted not to leak across the bore; the other types cannot always be depended upon in this respect. The stopcock used for this type of work is illustrated in figure 9.

### 6. PUMPS, AUXILIARY LINES

There are six pumps connected to this apparatus. One pump is the automatic mercury-displacement unit already mentioned. This acts as a backing pump to one of the two mercury-vapor pumps connected to the apparatus. The second mercury-vapor pump is connected near the differential manometer, so that it may be used when this section of the apparatus is isolated for a purity test. Both of the mercury-vapor pumps are connected so that they may be used to evacuate the apparatus as a whole, one working from each end if desired. Both are connected to permit the use of a Hyvac pump as the backing unit. A second Hyvac pump is used to operate the automatic mercury-displacement pump. A third Hyvac pump is assigned the general-utility role of moving mercury in the various reservoirs connected to the large burettes, the three McLeod gages, and also of reducing the pressure over liquid air surrounding the distilling tubes. This completes the census of the half-dozen pumps. It is readily seen that simultaneous procedures conducted with the apparatus may require the independent operation of each of the six pumps; and that if one were assigned a dual role, the procedures required might each have to wait their turn, which is never desirable and often impossible.

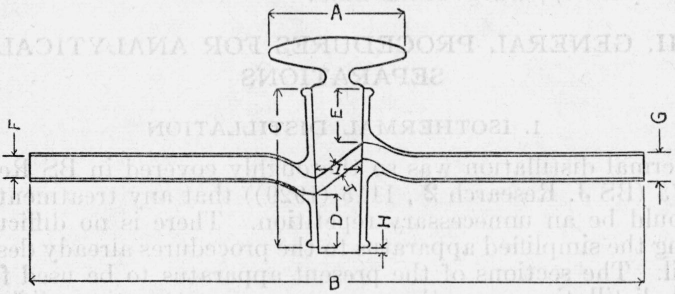

FIGURE 9.—*Drawing of stopcock for parts of apparatus subjected to low pressures.*

Dimensions in millimeters: *A*, approximately 42 to 44; *B*, approximately 200; *C*, approximately 47 to 49; *D*, 15 to 17; *E*, 15 to 17; *F*, 7; *G*, 10; *H*, 1 to 2; *I*, 15; *J*, 3.5.

Key and barrel must be finely ground to match perfectly. Only finest grade of high-vacuum grinding is acceptable. Glass should be thoroughly annealed before grinding. Ground surfaces must be free from scratches, chips, or striations. Bores of key and barrel must coincide and be free from chipping. Key to be hollow blown and free from pinholes where insert tube is sealed. Cock to be supplied without lubricant, oil, wax, or other dressing, and free from grinding compound. Key to be wrapped in tissue. Entire cock to be made of the same kind of glass. Put no trade marks, maker's name, other markings, raised rings or other mold or tool marks upon barrel. Put no pencil marks on grindings. Outlet tubes to be straight when 20 millimeters away from barrel, and on the same horizontal axis. Only finest workmanship throughout is acceptable.

The general-utility Hyvac pump is connected to a manifold which extends the entire length of the apparatus, with T-connections dropped to the desired points. A second manifold connects another

Hyvac pump to the two mercury-vapor pumps. The exhausts of all Hyvac pumps are piped to a manifold that discharges mercury vapor to the outside air.

### 7. APPARATUS SUPPORT

The whole apparatus is mounted on an iron frame constructed from ½-inch rod. This is mounted on the bench with flanges and braced with diagonal pieces at the back to prevent rocking. The whole is sufficiently rigid to eliminate the necessity of expansion joints in the glass connections. The tubing is held by comparatively few small cast clamps which are in turn held by standard V-clamp holders. Wing-tipped bolts have been replaced with hexagon-tipped bolts to fasten the clamp holders to the frame; this conserves space. The reservoirs containing mercury are mounted in plaster in special forms. We have used this type of mounting for over 20 years and find it very satisfactory for apparatus of this kind.

## III. GENERAL PROCEDURES FOR ANALYTICAL SEPARATIONS

### 1. ISOTHERMAL DISTILLATION

Isothermal distillation was so thoroughly covered in BS Research Paper 75 (BS J. Research **2** , 1145 (1929)) that any treatment given here would be an unnecessary repetition. There is no difficulty in adjusting the simplified apparatus to the procedures already described in detail. The sections of the present apparatus to be used for isothermal distillations are the gas-measurement section, differential manometer, and distilling-tube section. The uncondensed fractions can be collected with the automatic displacement pump, unless the operator has the good fortune to have liquid hydrogen at his disposal.

### 2. RECTIFICATION

If the amount of sample available is sufficiently large, preferably great enough to yield about 30 ml of liquid for distillation, the separation can best be conducted in the rectifying columns. The third column (*R3*) is designed to handle 30 ml of condensate; the fourth (*R4*) will operate with 2 to 10 ml of condensate. In addition to one of these two rectifying columns, the condensers, receivers, manometers, burets, and differential manometer, in a predetermined combination, may be employed. There are several procedures which can be used. They will be outlined separately.

*Procedure 1.*—This is the simplest choice, and is the kind of procedure generally used in this type of analysis. It has been discussed at length by Podbielniak, McMillan, and others.[10] As applied to the present apparatus, it is as follows: The sample to be analyzed is introduced (prior to measurement) into the evacuated apparatus at the inlet of the boiling pot (not at the top of the column as usual) and there condensed at the temperature of liquid air. The portion which does not condense at this temperature passes up the column and through the condenser at the top, which is also cooled by liquid air, at a temperature several degrees lower than that of the bottom pot. Thence it is allowed to escape very slowly through the barely opened

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[10] W. J. Podbielniak, Ind. Eng. Chem., Anal. Ed. **3**, 177 (1931). W. A. McMillan, J. Inst. Petrol. Tech. **22**, 616–45 (1936).

needle valve, *V1* (fig. 8), into one of the evacuated receivers (*F4*). The pressure in the condenser of the rectifier is registered on the manometer, *M2*, and that within the receiver is registered on the barometric manometer, *M3*. During this operation the rectifier becomes charged with reflux from the condenser at the top. The contact point of manometer *M2* is adjusted to the desired distilling pressure, usually atmospheric, and the distillation is allowed to proceed smoothly while readings of the condenser temperature and receiver pressure are taken simultaneously. The isobaric condition is maintained by adding liquid air to the jacket of the condenser, and such adjustment of valve *V1* as can be made without upsetting the condenser temperature and the amount of reflux in the column. (This valve affords a variable orifice between the column outlet and the receiver, and is placed *between* the two manometers. It is a Stimson type vacuum-packed valve with an extremely fine-pitched thread on the stem and a graduated handle.) The heat input of the boiling pot offers the third control of the operation of the column.

As one component boils off, the distillate ceases to enter the receiver and the condenser temperature slowly rises until it has reached the boiling point of the component next in order, at the pressure selected for distillation. If the drop counter indicates that the column is running dry during the separation of one component, valve *V1* is closed, the condenser temperature adjusted, the rate of boiling in the pot is increased, and, when reflux is reestablished, the distillate is again allowed to enter the receiver. The rate of distillation and reflux ratio will be determined by the nature of the mixture to be separated. In general, reflux ratios of about 10 to 1 are used, but it must be remembered that sharper separations are achieved by increasing this ratio and removing the distillate very slowly from the condenser.

At the end of this procedure, the observed condenser temperatures are plotted with respect to the corresponding receiver pressures. The latter are, of course, direct measures of the volume of distillate in terms of pressure within a fixed volume, assuming that the temperature of the receiver has remained constant or is corrected for; while the former are measures of composition in terms of the boiling points of the various components at the selected isobaric condition. The resulting curve would be a very sharp stairstep, with all vertical risers at right angles to the horizontal treads, *if* the separation were perfect. If the boiling points of the components are satisfactorily spread apart, a reasonably good stairstep curve will in fact be obtained. If the boiling points are too close, the curve which results must be subjected to mathematical analysis. In doubtful cases, such analysis must needs invoke a geometrical thaumaturgy that leaves one in some doubt as to just what the facts are. This has been the experience of many investigators when dealing with complex mixtures containing saturated, unsaturated, and aromatic hydrocarbons, boiling from about −40° C to slightly above 0° C. We must frankly admit that this procedure is good as far as it goes, but that it does not achieve the distance usually desired. Aside from the objection mentioned, there is the further objection that some methane, if present (and it usually is), will enter the receiver with the nitrogen and other lower-boiling gases, and cannot fully be accounted for unless separately determined in this fraction, usually by a volumetric combustion. The procedure is satisfactory for separating very simple mixtures, such as methane, ethane, propane, and butanes, provided the column has the efficiency of at least 30 theoretical plates.

*Procedure 2.*—This is a simple modification of procedure 1, and is designed to eliminate the objection in the separation of methane noted in the previous procedure. The first procedure is followed as before until the temperature of the condenser clearly indicates the removal of nitrogen and other uncondensed gases. The receiver is then shut off, a portion of the distillate is removed for analysis by combustion, and a correction is made on the plotted curve for the change in receiver pressure. The portion for combustion analysis is quickly removed by connecting the receiver to the 1,000-ml bulb of the gas-measurement section, using this bulb for a pump; or the automatic displacement pump can be used for this purpose.

*Procedure 3.*—This differs from the previous procedures in the following respects. Instead of allowing the condensable fractions of the distillate to enter the receiver, the separated components can be condensed in the series of condensers, and thence vaporized into the receiver one after the other at the end of the distillation. Since this entire operation may be done in a relatively short time, a correction for receiver temperature is usually unnecessary. In transferring the condensed distillates to the receiver, the procedure is as follows: Condensate in *C1* (fig. 8) is vaporized into *F4* and the pressure noted on *M3*. Condensate in *C2* is transferred to *C1*, *C2* is closed, and condensate now in *C1* is vaporized into *F4*, and so on. The volume of *F4* and connections thus remains fixed.

*Procedure 4.*—This is a modification of procedure 3, and is designed to eliminate the guessing which is an undesirable feature of the previous procedures in many cases. The distillation is conducted as in procedure 2 until the uncondensed gases are removed. Thereafter, procedure 3 is used until the first separations are accomplished and the distillates are all secured as condensates in *C1* to *C5*, and in *D1* to *D5* if these tubes are needed as condensers. The data are now examined to determine which distillates are in need of further separation. These distillates are then transferred to *R3* and *R4* and again distilled in order according to a regular fractionating pattern, until a satisfactorily sharp separation of the components is obtained in every case. Thereafter procedure 3 is resumed, and the now reasonably pure components are vaporized and measured one at a time as before. The purity of each component should be tested by means of the differential saturation-pressure manometer, if the analysis is exacting. This is quite a different story from the relatively easy tasks required by the previous procedures, but unfortunately it seems to be the only way of obtaining the desired information when dealing with unobliging mixtures, provided, of course, the entire process is limited to the method of distillation. Since this procedure is exacting and time-consuming, it would seem desirable to explore the field further with the assistance of other physical methods, such as thermal conductivity, interferometry, measurement of saturation pressures, etc., with the idea of determining the composition of binary mixtures yielded by the rectifiers.

## IV. GENERAL PROCEDURES FOR PREPARATION OF PURE GASES

### 1. NEED FOR AN ADEQUATE ACCOUNT OF THE PREPARATION OF A PURE GAS

The preparation of a critically pure gas is difficult, and may well be the major task in an investigation of the chemical or physical properties of the gas. Because of the difficulty of preparing gases suitable for study, some investigators have accepted the products of other workers, together with the certification which might accompany them. Others, not so easily contented, have applied their own tests of purity to these products and corrected the eventual measurements as might seem desirable. Still a third group have rather liked the idea of producing their own gases, if merely for the privilege of obtaining a first-hand guess of how good or bad their material might be.

The literature abounds in various measurements of the properties of gases, and measurements of the same property cannot invariably be expected to agree. Without doubt, one of the chief reasons for this lies in the fact that equally well-performed measurements have been made upon substances of slightly different compositions appearing under the same label.

There are two stock phrases used to indicate the fact that a gas is pure. One is: "The gas was purified by fractional distillation." The other is: "The purity was established by an isothermal condensation." Either of these phrases seems to serve as a certificate of purity. The first is meaningless without adequate qualification; and the second, while worth-while, may nevertheless fail to prove the point.

Consider the first phrase. Before it means anything, one must know what type of distillation was used, what kind of apparatus was employed, what various precautions were taken during the procedure, how many distillations or rectifications at what temperatures and pressures were performed, what proportions of the total sample were discarded as initial distillates and final residues, and, above all, what impurities were or might have been present before the purification was begun. For example, suppose carbon monoxide, prepared from the reaction of formic and sulfuric acids, was said to be pure simply because it had been "purified by fractional distillation." If air dissolved in these two reagents had not been painstakingly removed prior to the generation of carbon monoxide, nitrogen would have been one impurity to be removed by distillation. Since the normal boiling points of nitrogen and carbon monoxide are about 0.5 degree apart, the purification of carbon monoxide by fractional distillation would be hopeless. The quoted claim for purity is accordingly insufficient. Another such example is the often cited purification of oxygen by fractional distillation. Oxygen generated chemically from reagents containing dissolved and occluded air will contain nitrogen. The nitrogen might be removed in an efficient rectifying column, but only with considerable effort attended by tremendous waste of the initial sample. On the other hand, its removal by plain distillation without rectification is doubtful. Certainly the stock phrase needs considerable amplification. In the end, if purification is effected solely by fractional distillation, the criterion of purity is usually stated only in terms of a boiling point (or boiling range) taken during the course of distillation. Since a quantitative determination of purity on this basis would impose severe restrictions upon the maintenance of pressure and the measurement of temperature, this would again call for considerable and detailed amplification of the old phrase "purified by fractional distillation."

The second phrase means a great deal more, but it is nevertheless true that constancy of pressure during isothermal condensation is not always a good criterion of purity. The physical limitations of this method (which has been used for years as the final word in such matters) were discussed by E. W. Washburn.[11]

It would seem, therefore, that it is not only difficult to prepare a critically pure gas, but also difficult to judge from published reports just how pure were the gases dealt with in various investigations.

We have initiated a program intended to measure the accuracy of methods of gas analysis. This work is to be done in a simple, direct way. First, pure gases will be prepared. Second, the purity of these gases will be determined to greater significance than can be measured by the analytical methods to be studied. Third, and finally, the gases will be analyzed by standard methods, and the comparison of the results with the known composition of the sample will thus give a direct measure of the accuracy of the analytical methods. For this reason we shall have occasion from time to time to certify the purity of gases used in these and similar investigations. It seems desirable to place on record a description of the apparatus and general procedures used in the purification of such gases.

## 2. GENERAL PROCEDURES

The complete previous history of a gas to be purified by distillation should be known in order to formulate a list of the known and suspected impurities occurring with it and so plan the actual procedure of distillation. The gas may occur as a natural product in mixture with other gases, as a concentrate from some physical or chemical process, or as the result of a deliberately planned chemical reaction in the laboratory. In the latter event, the first stage of purification is to plan the generating apparatus and procedure with the object of eliminating any gases dissolved or occluded in liquid or solid reagents used for generation or preliminary purification, provided that such gases have boiling points near that of the gas to be purified. This may usually be done by evacuation and simultaneous displacement with another gas which *can* be eliminated later, or by vacuum sublimation. An example of such technique has been described.[12] Liquid reagents are greatly to be preferred from this viewpoint; and if solid reagents are used, it may sometimes be necessary to dissolve them, displace the dissolved gas, and then evaporate the solvent. If solid catalysts are used at elevated temperatures, an extremely thorough and prolonged evacuation at a temperature higher than will exist during the subsequent reaction is in order. Such evacuation should always be continued until, with the vacuum pump shut off, no significant amount of adsorbed or occluded gas is given off during a period of longer duration than will later be required for the generation of the gas. Such a procedure may take weeks.

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[11] *Constancy of pressure during isothermal condensation or vaporization as a criterion of purity*, Z. physik. Chem. (Cohen-Festband), p. 592 (1927).

[12] Martin Shepherd, E. R. Weaver, and S. F. Pickering, J. Research NBS **22**, 301 (1939) RP1182.

When the gas is to be generated in a separate apparatus, it is advisable to connect this directly to the distillation apparatus without rubber connections so that the whole will constitute a complete closed unit. The gas may then be taken in through one of the two interchangeable joints, at the fifth distilling tube or above the third condenser (fig. 8). The sections of the apparatus to be used for the purification are: rectifiers, condensers, receivers, differential manometer, and possibly the high-pressure transfer unit.

All parts of the apparatus involved in the purification are thoroughly evacuated until the pressure registered on the McLeod manometer is not over 0.0001 mm Hg after the vacuum pumps have been shut off overnight. The two mercury-vapor pumps are connected to the source of cooling water through a pressure regulator and by means of copper tubing cemented to the glass condensers of the pumps. The backing pump is connected to a large glass reservoir. This arrangement permits the safe operation of the pumps overnight, which greatly decreases the working time required for the preliminary evacuation. Even so, 70 to 150 hours are usually required for satisfactory evacuation. It should be remembered that glass and, in particular, the metal of the high-pressure transfer unit, liberate adsorbed gases grudgingly.

After the initial evacuation, the gas to be purified is condensed directly into the boiling pot of *R1* (fig. 8). The temperature of the top condenser of *R1* is lowered somewhat below the boiling point of the gas to be purified (at the selected distilling pressure), and heat is applied to the boiling pot. When the column is properly charged and is refluxing liberally, the outlet is opened slowly through the valve, *V1*, to the vacuum pump. The initial distillate is discarded through this pump until the temperature within the condenser at the top of the column (hereinafter called the distilling temperature) has remained constant for at least 15 minutes under the isobaric condition chosen, the distillate having been discarded at a rate not greater than 0.5 liter per minute during this period. If this condition is obtained before one-twentieth of the liquid has been evaporated from the boiling pot, the distillate is nevertheless discarded until at least this much of the original condensate has disappeared. If the amount of gas on hand is abundant, it is best to discard the first one-tenth of the condensate at this time. In measuring the initial rates of distillation, the distillate is taken into the evacuated glass reservoir connected to the backing pump, which is provided with a barometric manometer. If the capacity of this reservoir is exceeded, it may be quickly evacuated again to several millimeters pressure and so refilled.

The distillate is next allowed to enter the large receivers (*F1* to *F5*), *one at a time,* and the distillation may proceed thus until the distilling temperature begins to rise very slightly. The particular receiver in use at the moment is closed, and another is opened until the change in the distilling temperature gives positive evidence of the presence of a higher-boiling component in the distillate. If the fluctuation of distilling temperature has been momentary, the desired gas may be saved by this procedure; if the change of temperature was permanent, the distillate collected in the trial receiver is discarded, together with the rest of the residue in the boiling pot. The whole apparatus is then thoroughly evacuated. After evacuation, the distillate is admitted from one of the receivers until the pressure within the apparatus reaches 5 to 10 mm Hg. This washes the glass walls with approximately pure gas, a technique of flushing which is followed throughout the preparation of the gas. The apparatus is again evacuated, and is then ready for the second rectification.

The distillate from all receivers is now condensed in the boiling pot of *R1*, after which this rectifier is closed and the rest of the apparatus and the receivers are thoroughly evacuated. The condenser of *R1* is then cooled, heat is again applied to the boiling pot, the column is charged, and reflux is established. During the entire course of the rectification which follows, the drop counter of *R1* should discharge about 2 drops per second, the distillate should be taken away at a rate not greater than 20 liters per hour, and the heat input balanced to preserve this condition. The first one-twentieth of the entire condensate is discarded through the vacuum pump; and if the distilling temperature remains constant under the selected isobaric condition, the distillate is diverted to condenser *C2* until 1 ml has been collected as a liquid. Then *C2* is closed and the distillate is diverted to receiver *F1*. While *F1* is filling, the isolated condenser section is evacuated in order to remove gas in the connecting lines. When the receiver *F1* is filled to a pressure about 10 mm less than the distilling pressure, it is closed and about 1 ml of distillate is collected as a condensate in *C3*. This condenser is then isolated, the distillate from *R1* is diverted into *F2*, and the line leading to the isolated condenser section is simultaneously evacuated. When *F2* has been filled as was *F1*, it is closed and a second 1-ml portion of distillate is condensed in *C4*. This procedure is continued until the receivers contain successive portions of the distillate and the condensers contain successive small portions of condensed distillate taken after the filling of each receiver. The distilling tubes may be used as condensers if needed. When the distilling temperature begins to rise, the distillate and residue in the boiling pot are discarded. If the distilling temperature does not rise, the last one-twentieth of the original condensate is nevertheless discarded as residue.

The differential manometer is now used to compare the saturation pressures of the distillate collected in *C2* (initial distillate collected before any gas was stored in the receivers) with that of the last distillate taken as a condensate (final residue). If the saturation pressures of these two are satisfactorily equal, and so indicate the desired degree of purity, the gas in all the receivers may be considered good. If this is not the case, further exploration is made of the condensed distillates, and the resulting $\Delta p$ measurements will determine which receivers contain gas suitable for further purification or which may be sufficiently pure.

If further rectifications are necessary, the procedure is exactly the same as for the second rectification, with the following possible exceptions. Either *R1* or *R2* may be used. The latter has the advantage of being all glass, and thus eliminates the slight uncertainty associated with adsorption on the carborundum coating of *R1*. It is not quite so efficient a rectifier, however. In a final rectification, the distillate may be collected as a condensate in *C1*. Small portions of initial distillate and final residue are to be taken for test by the differential saturation-pressure method. This procedure has the advantage of eliminating again small uncertainties associated with adsorption on the large surface of the glass walls of the 22-liter receivers. True, the uncertainties associated with sorption-desorption throughout the apparatus are minimized by the washing and evacuating technique rigorously followed throughout; but for the most exacting work, collection of the distillate in *C1* is preferable.

It is recognized that these general procedures may have to be modified to meet the peculiar demands of some mixtures of gases. If so, such modifications can be noted as necessary in following reports. The $\Delta p$ measurements obtained by the differential saturation-pressure manometer will always be noted in any published certification of purity.

### 3. TRANSFER AND STORAGE OF PURE GASES

Morley once said that the difficulty was not in thoroughly drying a vessel, but in keeping it dry. The same thought will apply to a pure gas, although the decided difficulty of *getting* it pure will justify a real effort to keep it so. For this reason, the technique of transfer by condensation and subsequent vaporization has been selected as the preferred procedure—even when this involves the use of liquid hydrogen as the cooling agent. In the absence of an adequate condensing bath, mercury displacement is employed.

Some type of storage container must usually be interposed between the purification apparatus and that in which the gas is to be eventually used. If this container cannot be dispensed with, it must be a good one and properly used. The storage reservoir must be sealed directly to the purification apparatus, either by a fused-glass joint or by means of a ground-glass joint capable of withstanding high vacuum. The interchangeable joints[13] are very convenient and satisfactory if secured by a suitable thermoplastic cement of negligible vapor pressure. (Some of the interchangeable joints are satisfactory with a high-vacuum lubricant.) It is desirable to have the storage container joined to the apparatus during the purification of the gas. This gives the same opportunity that exists in the purification apparatus of flushing the storage vessel with successive portions of the gas as this becomes purer at each stage of rectification, with evacuation between such flushings. In any event, a final flushing with the pure gas and subsequent evacuation should precede the actual transfer of the gas to be stored.

The storage reservoir should be connected to the apparatus into which it is to deliver the gas for use with the same care that was taken in connecting it to the purification apparatus. The apparatus to be used for making the measurements of the properties of the gas must likewise be prepared with the same care used in preparing the purification apparatus. These obvious facts are often overlooked, especially by investigators who have not prepared the gases themselves.

Storage reservoirs must be equipped with stopcocks of the same quality as those used in the purification apparatus. The reservoirs may be of two types—those that deliver the gas under positive pressure, and those from which the gas must be removed by condensation or mercury displacement. The first group includes metal cylinders. If these are used, the walls should be smooth and free from dirt and water. The valves must be of the diaphragm type or have special packing that will withstand high vacuum. (We have used the Stimson and Kerotest valves successfully.) The gas to be stored must not react with the metal of the reservoir.

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[13] Commercial Standard CS21-39, Interchangeable Ground-Glass Joints, Stopcocks, and Stoppers, Fourth Edition.

On the whole, glass makes a better container when purity is at stake. Figure 10 illustrates four of the types of storage containers ordinarily used. Number 1 is the most useful, although somewhat heavy and not easily managed by one person. It consists of two inclined reservoirs mounted on an angle-iron frame. The lower reservoir holds approximately 2 liters of gas under atmospheric conditions. The stopcock at the top has a 120° bore, and one outlet is equipped with an interchangeable joint (male member). A mercury seal is placed in the two upper leads whenever gas is stored. The cock at the top of the upper reservoir may be connected to vacuum or air. A third cock at the bottom of the lower reservoir arrests the flow of mercury. Number 2 of figure 10 is a greatly cheapened and more portable form, made from a heavy-walled filter flask of 2-liter capacity. The operator must carefully watch the supply of mercury in the small reservoir at the top, and be sure that no vortex forms when this is admitted to the flask. Otherwise it is not apt to give trouble. Number 3–3 is still another form using mercury displacement. The flasks are 5-liter, heavy-walled, spherical, boiling flasks and the pair are mounted independently on convenient tripods, so that they may travel as separate units. One may be used as a mercury reservoir, the other as a gas reservoir. Number 4 is a 5-liter boiling flask, necked down and terminated with the newer type of stopcock which was previously noted at the top of glass-stoppered U-tubes. An interchangeable joint affords a convenient means of connecting. Gas is withdrawn from this container by condensation or mercury displacement, the mercury in this case being in the attached apparatus. Variations on this general theme will occur to suit the individual taste.

## V. COMMENT ON REPRODUCTION OF THIS APPARATUS

In presenting this information, it is realized that instructions concerning the actual construction of the apparatus have been very general. Although a good idea has been given by the photographs and text, the exact duplication of the apparatus could scarcely be accomplished using the material here presented as the sole guide. In making the presentation so general, we have been acting on the strong conviction that no one will wish to reproduce the apparatus exactly as it stands. (In the event that is incorrect, the apparatus can be seen at our laboratory and the requisite number of detailed shop drawings made by the interested party.) It seems more than likely that any attempt to duplicate the apparatus would be largely in principle only, and sufficient information has been given for this. Aside from that, one's imagination is apt to be as good as another's.

WASHINGTON, December 30, 1940.

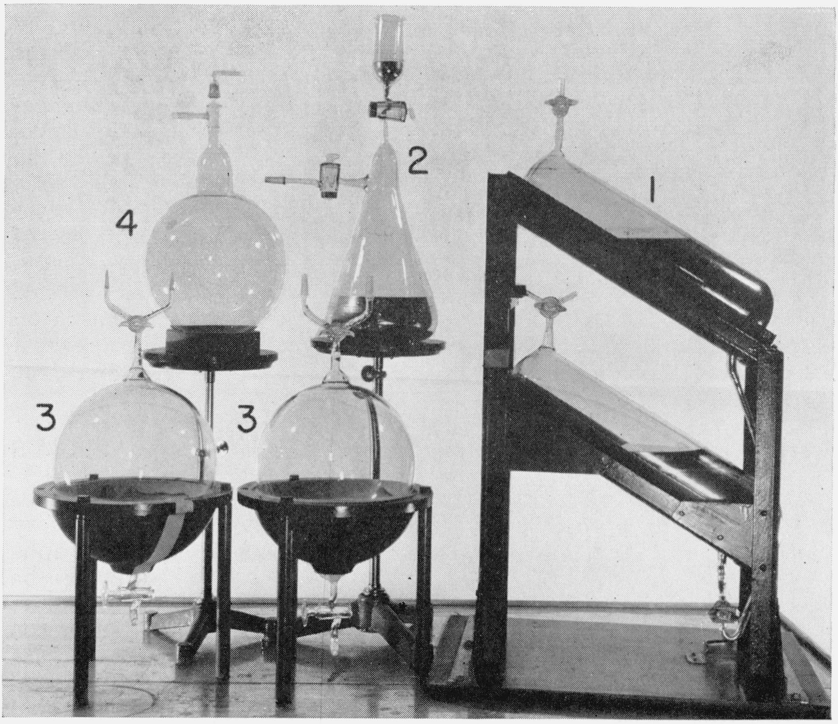

Figure 10.—*Storage reservoirs.*