

Characterization and Separation of Products

Direct Determination of Oxygen

In the analysis of oxygenated organic compounds, such as those obtained in gas synthesis and from hydrogenated coal, it has been customary to determine their oxygen contents by subtracting from 100 the sum of the percentages of all other elements present. Thus, the errors made in the analyses of the other constituents are accumulated in the value obtained for oxygen. To avoid such errors, a direct method of oxygen analysis has been developed, based on earlier work done here and abroad. Briefly, the method involves pyrolyzing the sample in a closed system and sweeping the products of pyrolysis through a carbon-packed reaction tube at 1,120° C. with a stream of oxygen-free nitrogen. In passing through the reaction tube, the oxygen-containing pyrolytic fragments are converted quantitatively into carbon monoxide, which is oxidized with iodine pentoxide. The resulting carbon dioxide is then absorbed in a measured excess of 0.05N alkali, and the excess is back-titrated with 0.025N acid after precipitation of the carbonate formed with barium chloride. Numerous data on pure oxygenated compounds, hydrocarbons, and miscellaneous substances indicate that results accurate to within ± 1 percent are obtained over a range of 0.05 to 50 percent oxygen, using 15- to 350-milligram samples and a total analysis time of 35 to 45 minutes. The apparatus (see fig. 34) is simple and serviceable and includes a reaction tube that permits easy and accurate handling of volatile and nonvolatile samples. The presence of nitrogen, chlorine, or iodine causes no difficulty, but sulfur leads to abnormally high results.

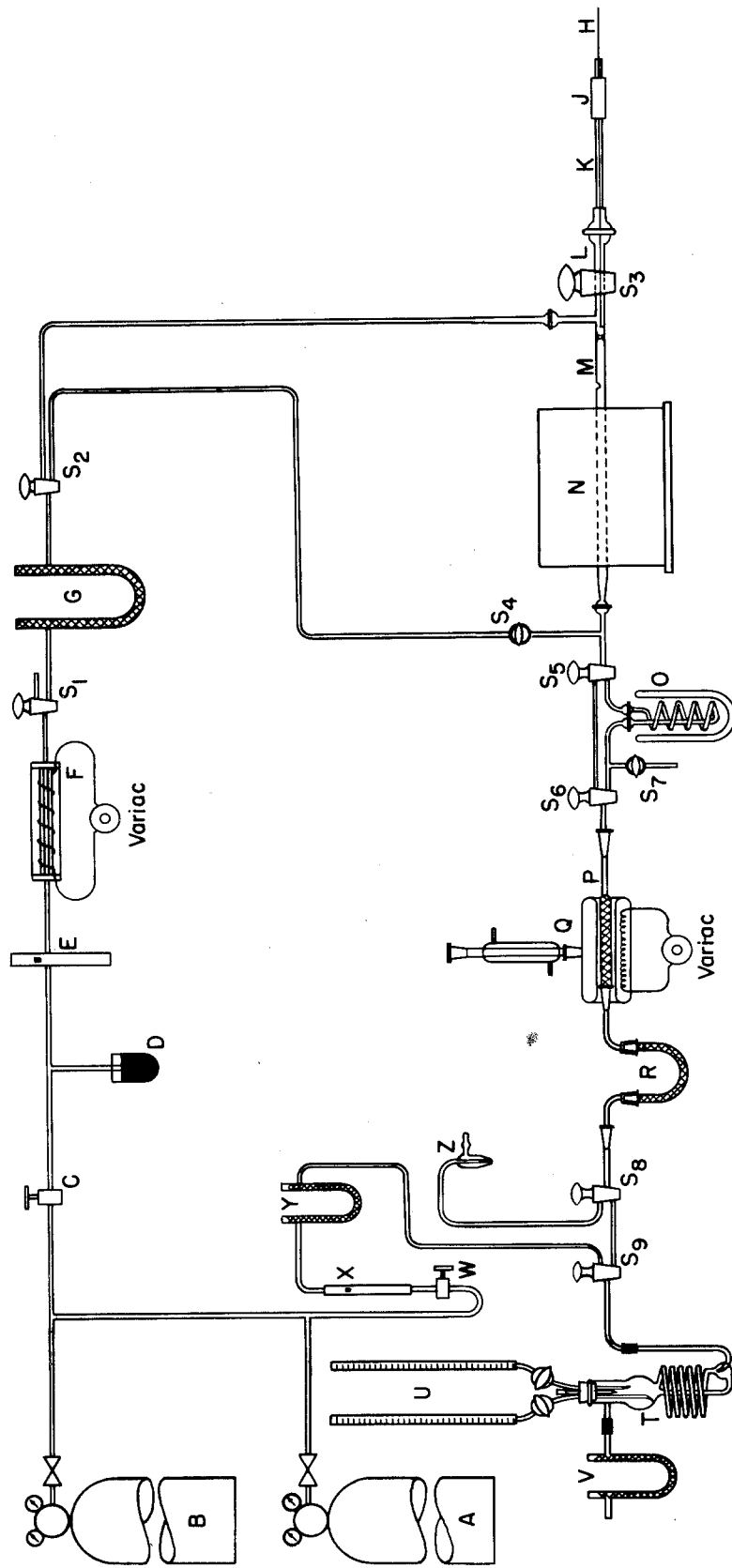
Tar Acids and Bases

The yield of tar acids, phenol in particular, from the hydrogenation of coal determines, in part, the value of the products from coal hydrogenation. The good mass balances obtained in the autoclaves, coupled with newly developed analytical techniques (see figs. 35, 36, and 37), make possible accurate analyses of the product from coal samples as small as or smaller than 50 grams.

Comparison of the phenol contents of the hydrogenation products from Western Kentucky and Wyoming coal showed that the relative concentration of phenol in the aqueous and oil products was independent of the composition of the coals. Three-quarters of the total phenol was in the oil layer; that layer comprised two-thirds of the liquid product.

To determine whether there are inadvertent losses of phenols in the current procedure for isolating the phenol fraction of coal-hydrogenation oils (see fig. 38), the recovery of phenol was checked by countercurrent distribution at different stages of the extraction procedure. The original sample was a Demonstration Plant product from hydrogenation of Lake DeSmet coal. Because of interfering substances, analysis of the various fractions was confined to phenol itself. The losses of higher homologs would, of course, be less than those of phenol. There appeared to be a significant loss of phenol as a result of acid washing and chloroform extraction of the acidified alkaline extracts. The losses, calculated by difference, were higher than those obtained by countercurrent-distribution analyses of the acid washings and spent aqueous liquor. The latter figures were probably only semiquantitative because of the very small concentration of phenol. The over-all loss of phenol in the extraction amounted to about 11 percent.

Complex formation between tar acids and tar bases was studied because of its possible effect on quantitative extraction of tar acids and bases from coal and its utilization in separating individual tar acids or bases from their mixtures. For this



- | | | |
|---|--|--------------------------------|
| A - Nitrogen-tank source | J - Guide block | S1 - S9 - Stopcocks |
| B - Hydrogen-tank source | K - Pusher-rod guide tube | T - CO ₂ absorber |
| C - Needle valve | L - Purging lock | U - Titrating burettes |
| D - Over-pressure blow-off | M - Reaction tube | V - Ascarite-filled guard tube |
| E - Rotameter | N - Reaction-tube furnace | W - Needle valve |
| F - Nitrogen-purification furnace | O - Liquid nitrogen-cooled trap | X - Rotameter |
| G - CO ₂ and H ₂ O absorber | P - I ₂ O ₅ oxidation tube | Y - Ascarite-filled guard tube |
| H - Pusher rod | Q - Oxidation-tube heater | Z - Flow-indicating bubbler |
| | R - Iodine absorber | |

Figure 34. - Schematic drawing of apparatus for direct determination of oxygen.

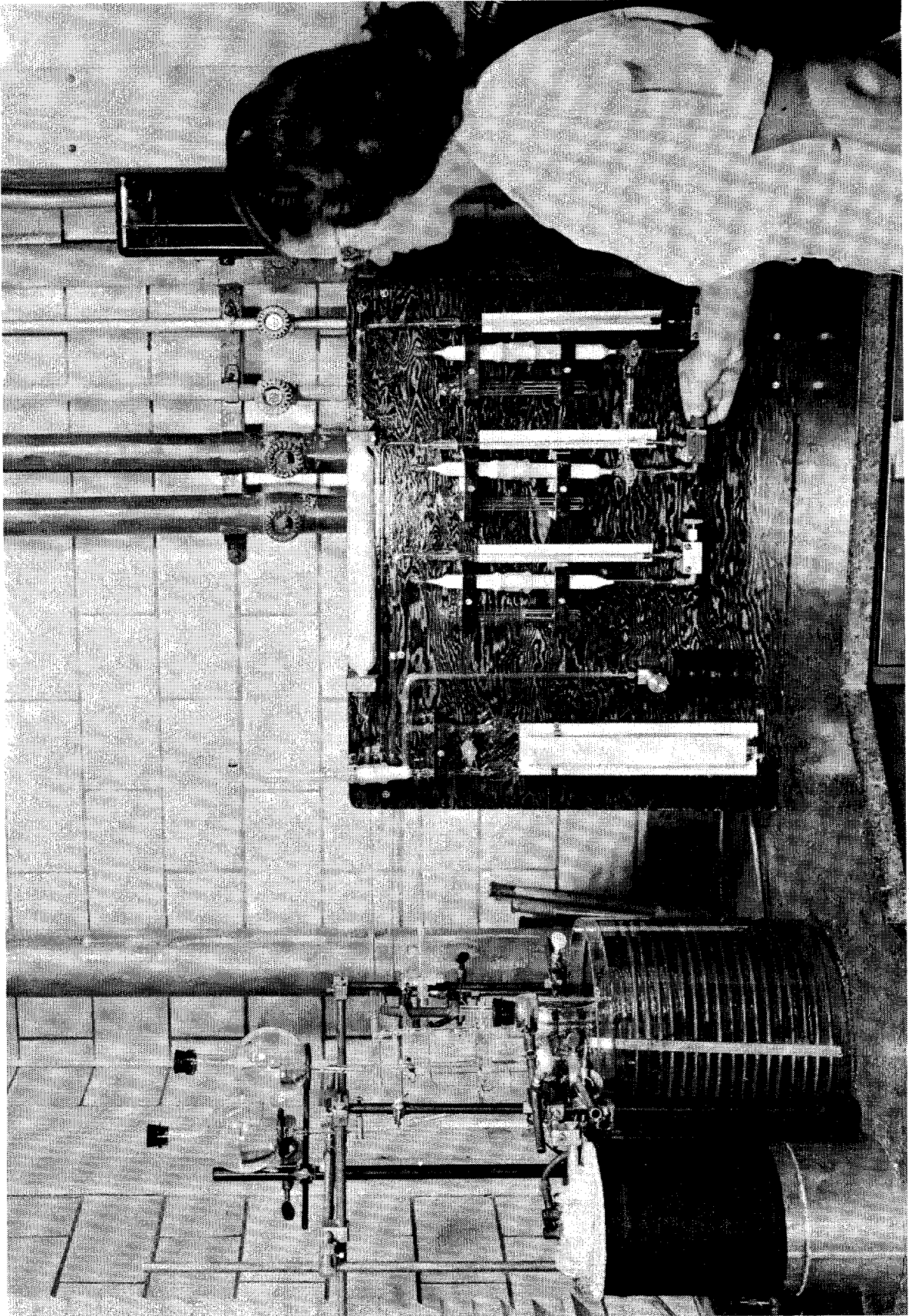


Figure 35. - Apparatus for determining equilibria in gaseous systems.

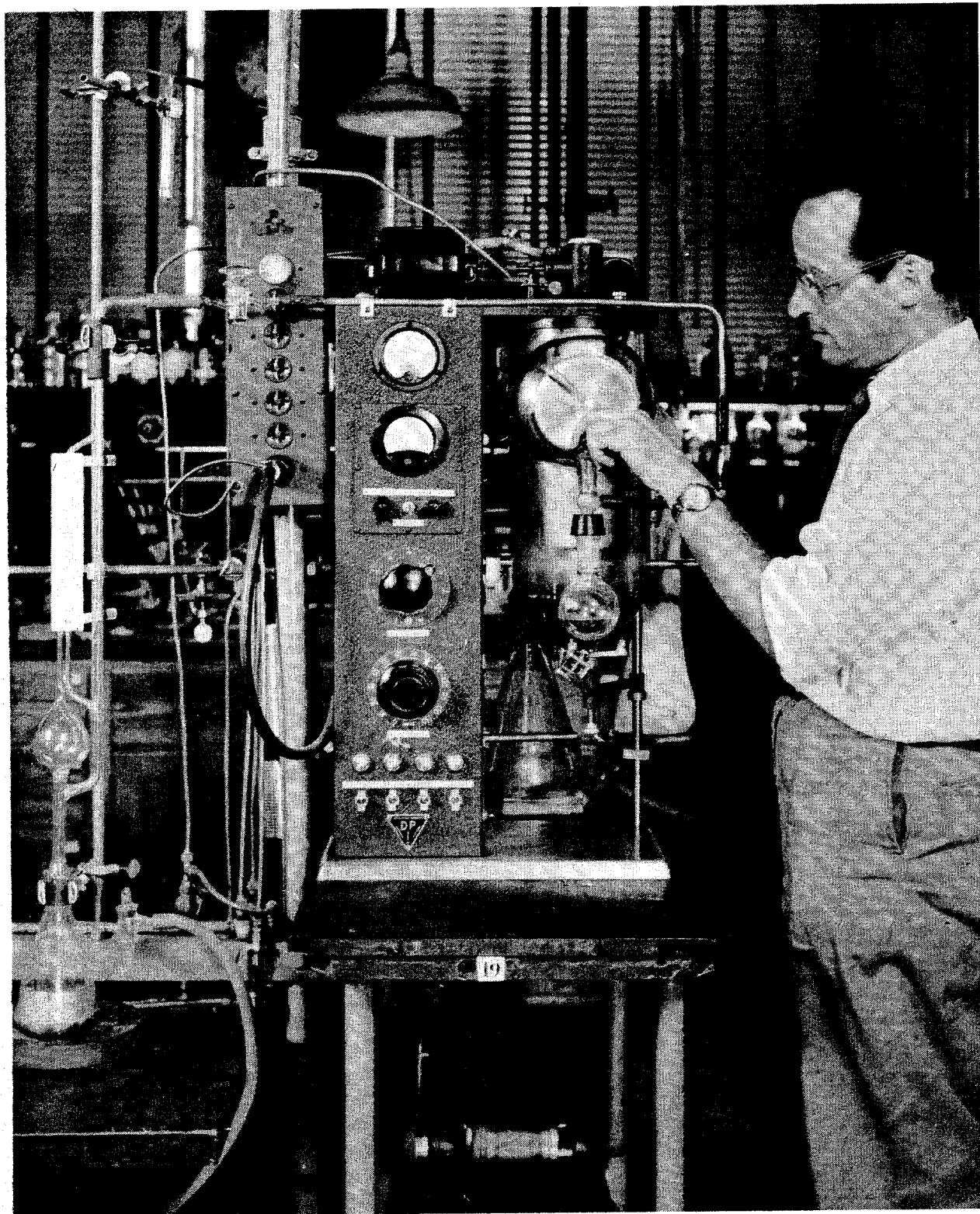


Figure 36. - Cyclic molecular still for isolating coronene.

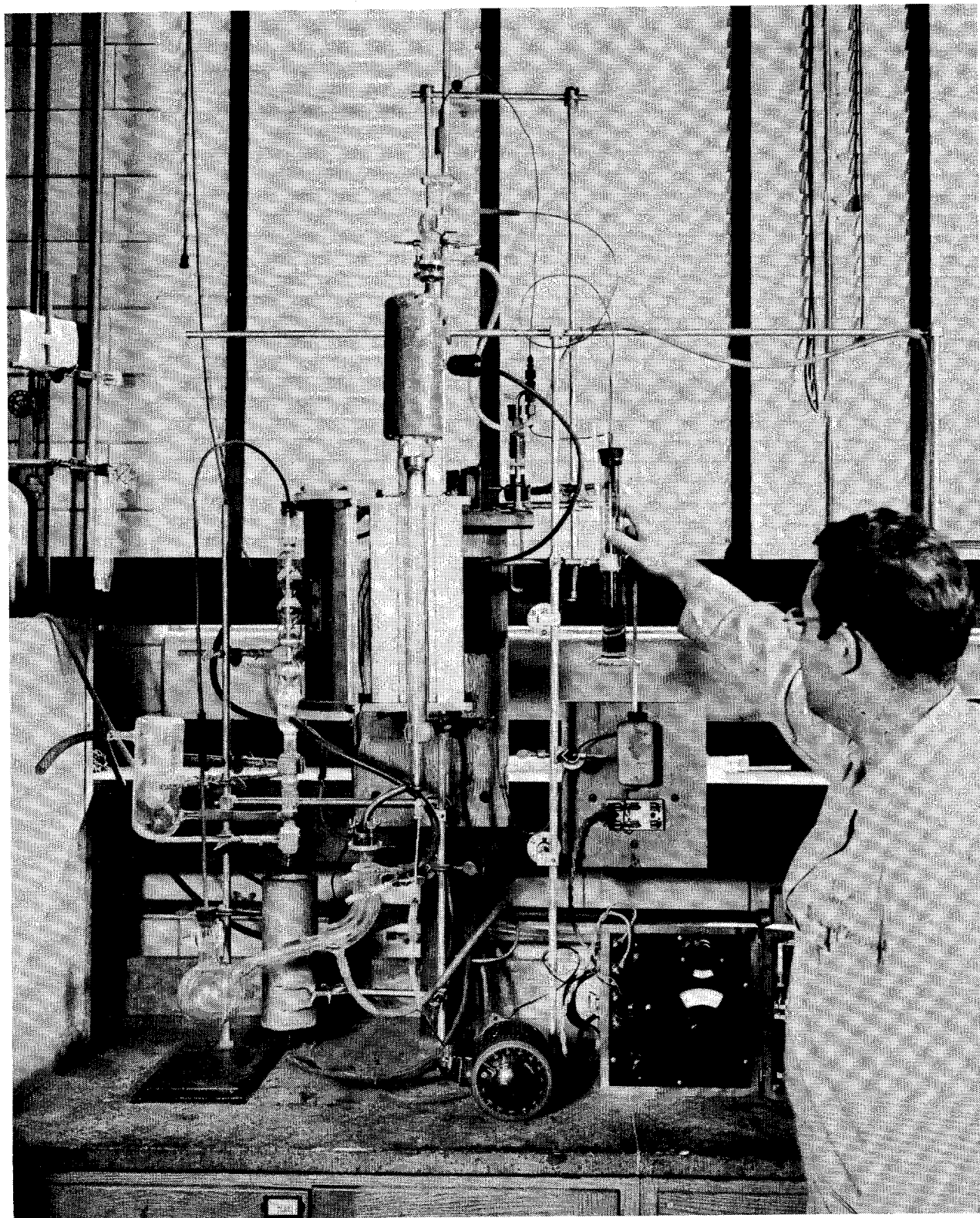


Figure 37. - Dehydrogenation apparatus.

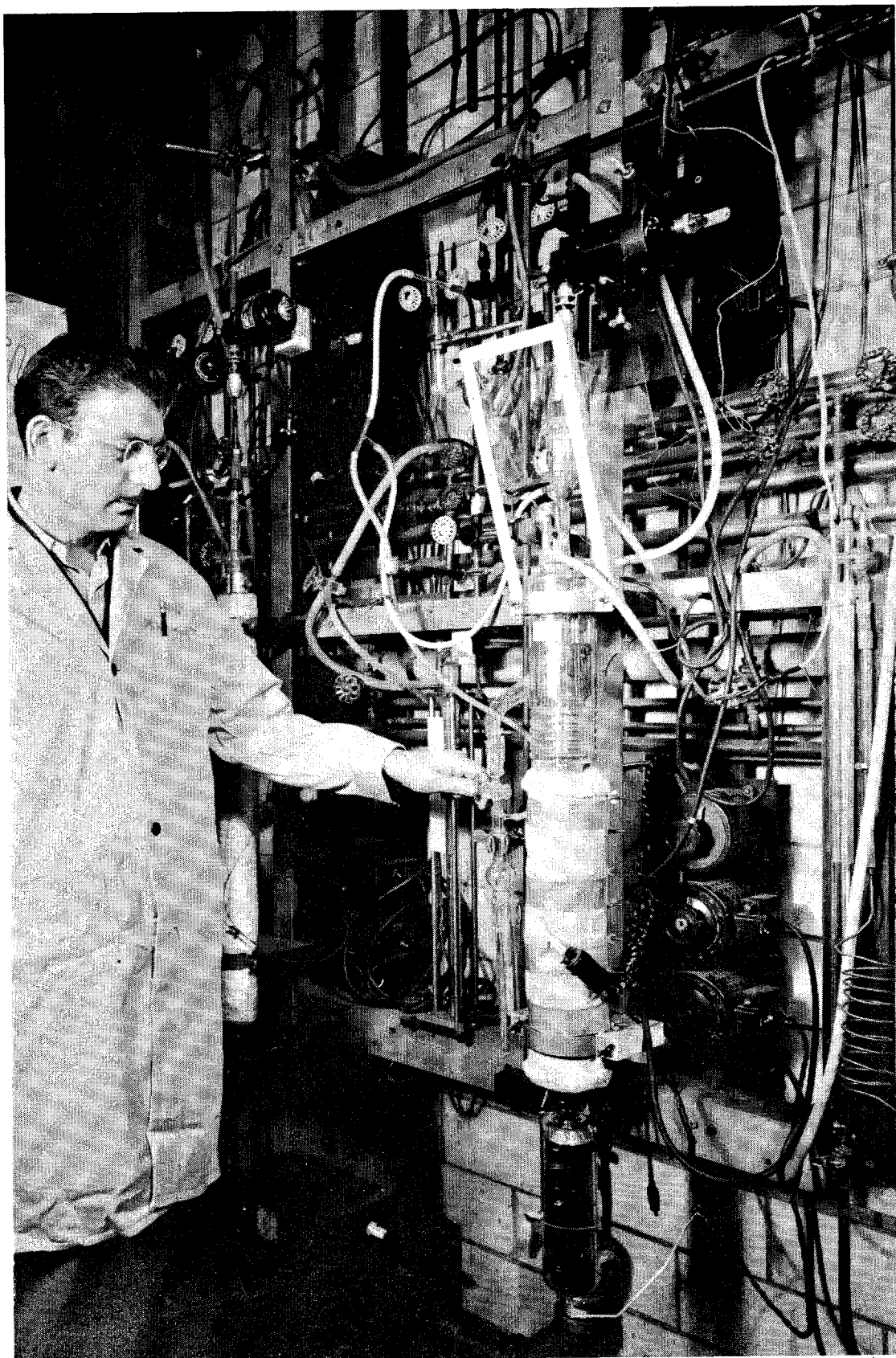


Figure 38. - Spinning-band column for phenol separation.

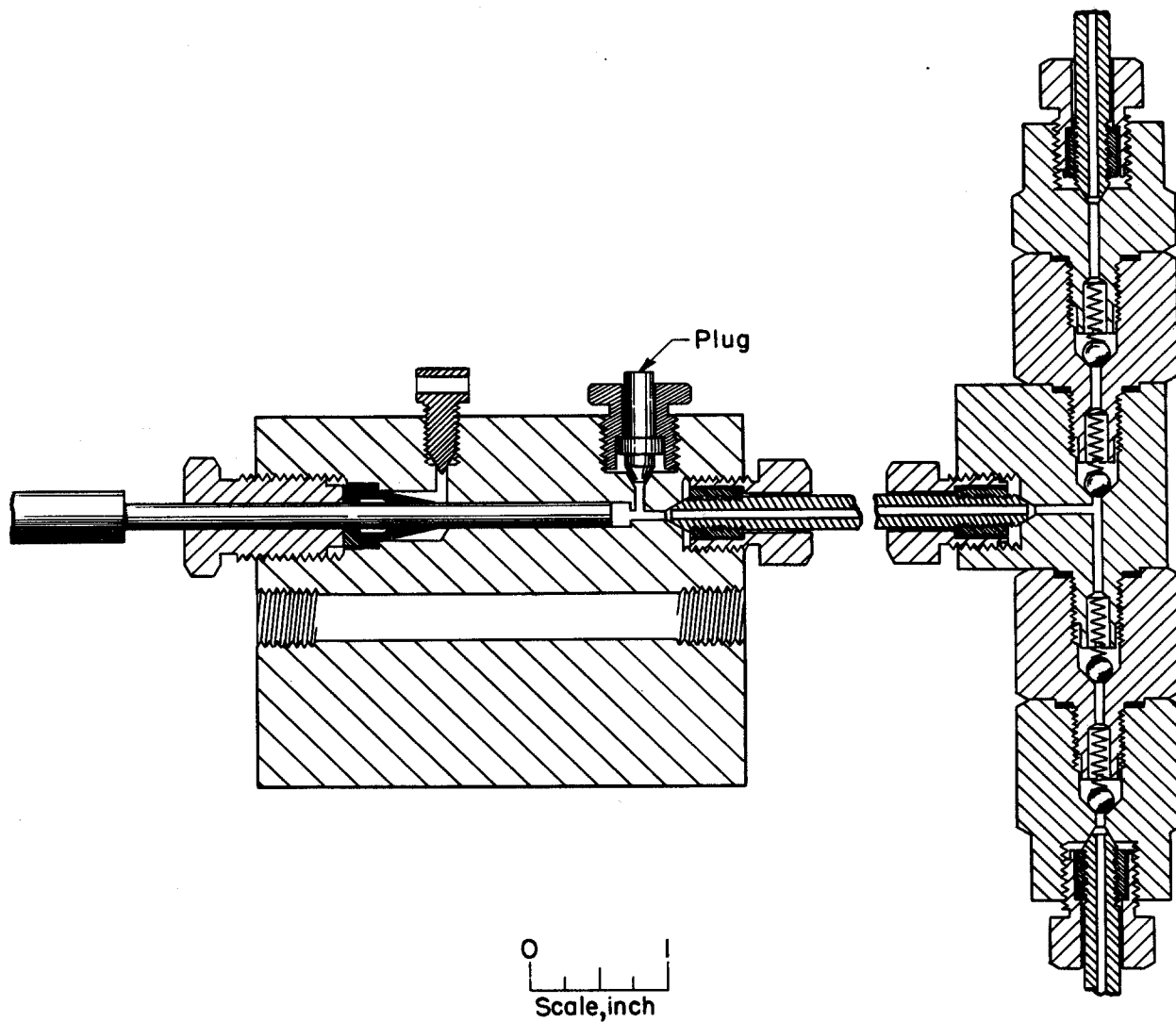


Figure 39. - High-pressure, low-volume pump.

purpose, aniline and the isomeric cresols were investigated in the system cyclohexane-water. It was found that complex formation in the aqueous phase is negligible. Also, the tendency of aniline and the cresols to form complexes is weak and should not interfere with separation of these two classes of compounds, particularly if their concentrations are maintained low during extraction. It may be noted also that the ratio of partition coefficients for a mixture of m- and p-cresol is only slightly higher in the presence of aniline than in its absence. Aniline would thus be only slightly efficacious in separating a mixture of m- and p-cresol. In a mixture of o-cresol with m- or p-cresol, aniline would actually hinder separation of these cresols.

High-Pressure Instrumentation

Many of the instruments needed in developmental work on coal hydrogenation at high pressures are not commercially available. Numerous improved and new techniques and devices had to be developed. These ranged from the modification, care, maintenance, and method of installation of commercial pumps to completely new designs and fabrication of connectors, sealing rings, pressure controllers, flow meters, and special product receivers.

High-Pressure Connections

Erection of a pilot plant for use at 7,500 p.s.i.g. led to design of a fitting in which a cinch is threaded on the tubing and sealed to it by silver soldering. Another fitting, developed to circumvent the silver soldering, utilizes a metallic gasket to effect a seal between the tubing end and the fitting. This connection is satisfactory for service at up to 12,000 p.s.i.g., provided the tubing is not under stress due to misalignment or subject to accidental displacement, which deforms the gasket and causes leakage. There is a chance that the cinch may be tightened too much in making the gasket seal, thus shearing the tubing at the root of the thread. In a third type of fitting, the tubing is turned down to the root diameter of a 1/4-40 thread for a short distance and threaded for the cinch. The cinch fits the turned-down portion of the tubing snugly and is thus in position to be sealed against the tube. Although more intricate than the cinch using the metal gasket, it was thought to be superior, in that it would be less subject to leakage due to thermal shock or accidental application of force to the tubing. This may be true, but no great difficulties have been encountered with the gasketed cinch, which is preferred because of its relative simplicity. The screwed cinch is used, however, when the tubing must be extended beyond the fitting for a dip tube, standpipe, or thermocouple well.

High-Pressure, Low-Volume Pump

The need for delivering small volumes of liquid at reproducible and constant rates led to development of the pump shown in figure 39. The hardened and polished plunger, of type 410 stainless steel, is soldered into the crosshead of a drill rod, which reciprocates in bronze bushings in the crosshead guide. The surface of the plunger is made as smooth and as uniformly cylindrical as possible to lengthen the life of the packing. If the pumped liquids were less reactive, harder structural materials could be used to increase the quality of the surface. The plunger is 1/8 inch in diameter and enters the pump body, which is drilled with a No. 30 drill (0.1285 inch). The pump body is of type 303 stainless steel to facilitate machining. The packing is a conical Teflon sleeve, which provides a tight fit on the plunger and is forced against it during the forward stroke. Double ball valves were used on both suction and discharge. The balls and valve bodies are stainless steel and the balls positively seated by phosphor-bronze wire springs. Neoprene gaskets are used between the parts of the valve assembly. The pump body and valves are tapped for commercially

available tubing fittings. Structural parts not in contact with the fluid being pumped are of mild carbon steel (C-1018).

This pump has been used to pump oil (S.A.E. No. 10 lubricating oil) into an accumulator to displace gas at a constant rate of about 215 cc./hr. and at a pressure of 4,000 p.s.i.g. So far the pump has had about 200 hours service in a series of 8-hour runs in a bench-scale unit. No maintenance of any kind has been required as yet, and the rate varies less than 0.1 cc./min., as determined by checking the volume delivered in a few minutes from a burette graduated in tenths of a cubic centimeter.

An identical pump was used for pumping 30 to 50 cc./hr. of solutions, of which methyl or ethyl alcohols were the solvents. Some trouble was caused by the combination of poor lubricating properties and occasional deposition of precipitated particles in the check valves. Occasionally an 8-hour run was made without tightening the packing nut or cleaning a check valve; but at worst the packing needed two adjustments during a run, and the check valves occasionally required cleaning. With alcohol alone, occasional adjustment of packing was the only maintenance required.

Sensitive Pressure Controller

An automatic, sensitive, pneumatic pressure controller has been developed for regulating the flow of hydrogen to a bench-scale, high-pressure hydrogenation unit. A schematic diagram of the controller is shown in figure 40. The sensing element is a 20-turn helix of pressure tubing rated at 20,000 p.s.i.g.; this tube gives much more movement than the conventional Bourdon tube and is suitable for use with hydrogen. The flapper of a nozzle-flapper combination is attached directly to the Bourdon tube, eliminating friction and drag in linkages, gears, and levers, the chief causes of lack of sensitivity in pressure controllers. Air nozzle 1 is small and can therefore be located close to the flapper for maximum sensitivity. The nozzle position is adjustable for controlling any pressure up to 20,000 p.s.i.g.

As the hydrogen pressure rises, the flapper approaches nozzle 1 and induces back pressure of air in the controller, expanding a light bellows, 2; this in turn shuts off an appreciably greater air leak, 3, and thus pressurizes a larger and sturdier bellows, 4. Attached to this bellows is a double-coned needle, 5, which is moved between two closely spaced escape orifices 6 and 7 connected to opposed air-drive cylinders 8 and 9. The cylinders are sealed by leather cups, which are attached to a rack extending between the cylinders. Air pressure in either cylinder pushes the rack, which drives a gear connected directly to the stem of the throttling valve. At the center position of needle 5, the pressure on the cylinders is equal, and the valve remains motionless until the large bellows 4 contracts or expands.

The usual air pressure (17 p.s.i.g.) may be changed by metering capillaries 10 to 13 when necessary. The rack contains two adjustable mechanical stops. One is set so that the throttling valve cannot be shut completely, preventing damage to the needle and seat. Manually operated valves, in series with it, are used for complete shut-off. The other stop, for maximum valve opening, is set for approximately twice the necessary flow.

With the original controller, a variation of 1.5 p.s.i. from the control point was sufficient to induce on-and-off action; however, the control point tended to drift slightly. In the final design, some sensitivity was sacrificed for greater stability. The present instrument, which was checked up to 10,000 p.s.i.g. on a gage tester, has a sensitivity of \pm 10 p.s.i. Air is metered to the cylinders through capillary tubing, giving a rather slow, deliberate action to prevent overshooting and cycling. One minor drawback is that close control of the air supply is necessary, since a pressure change of 1.5 or 2 p.s.i. would inactivate the controller.

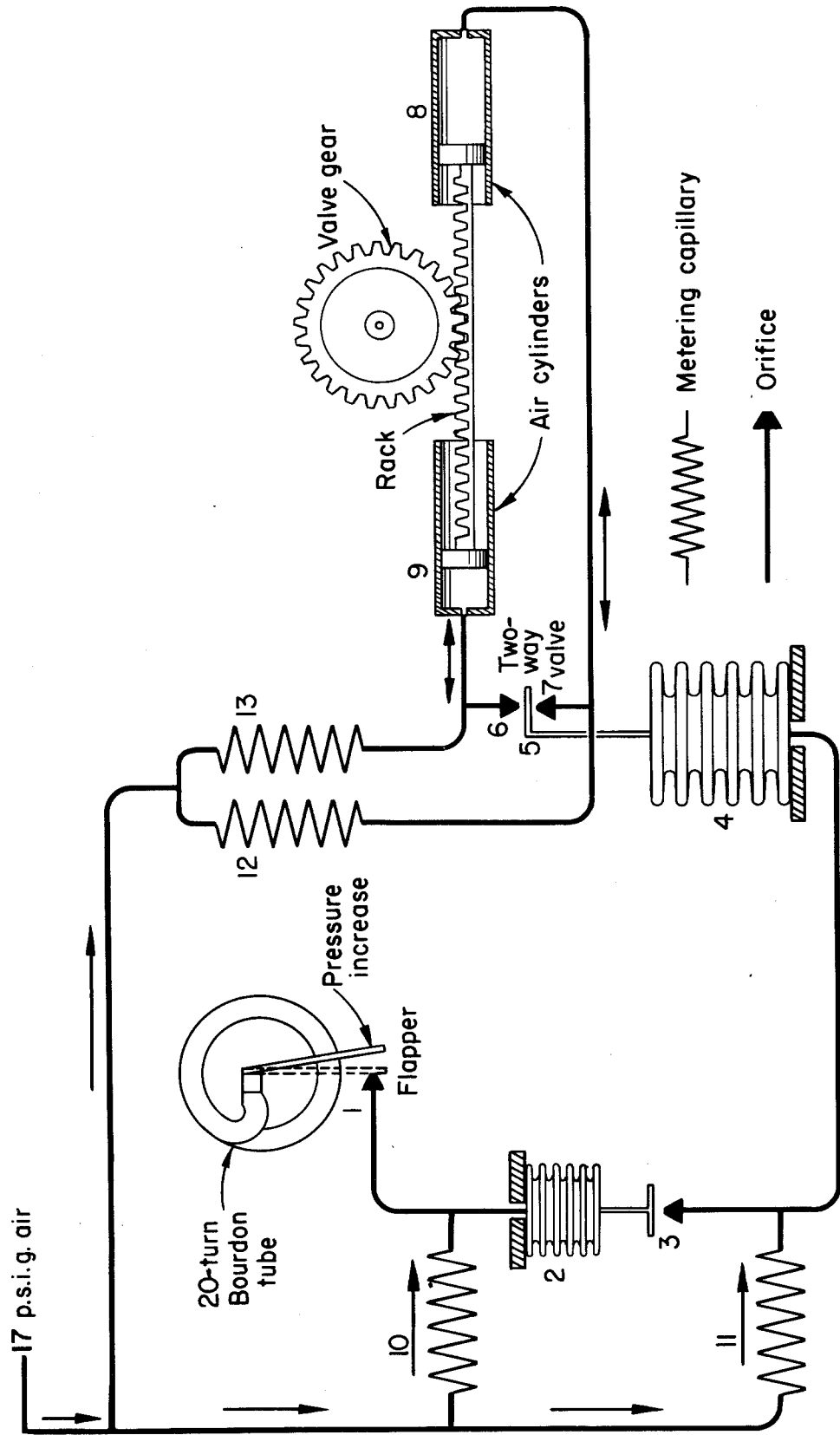


Figure 40. - Schematic diagram of pressure controller.

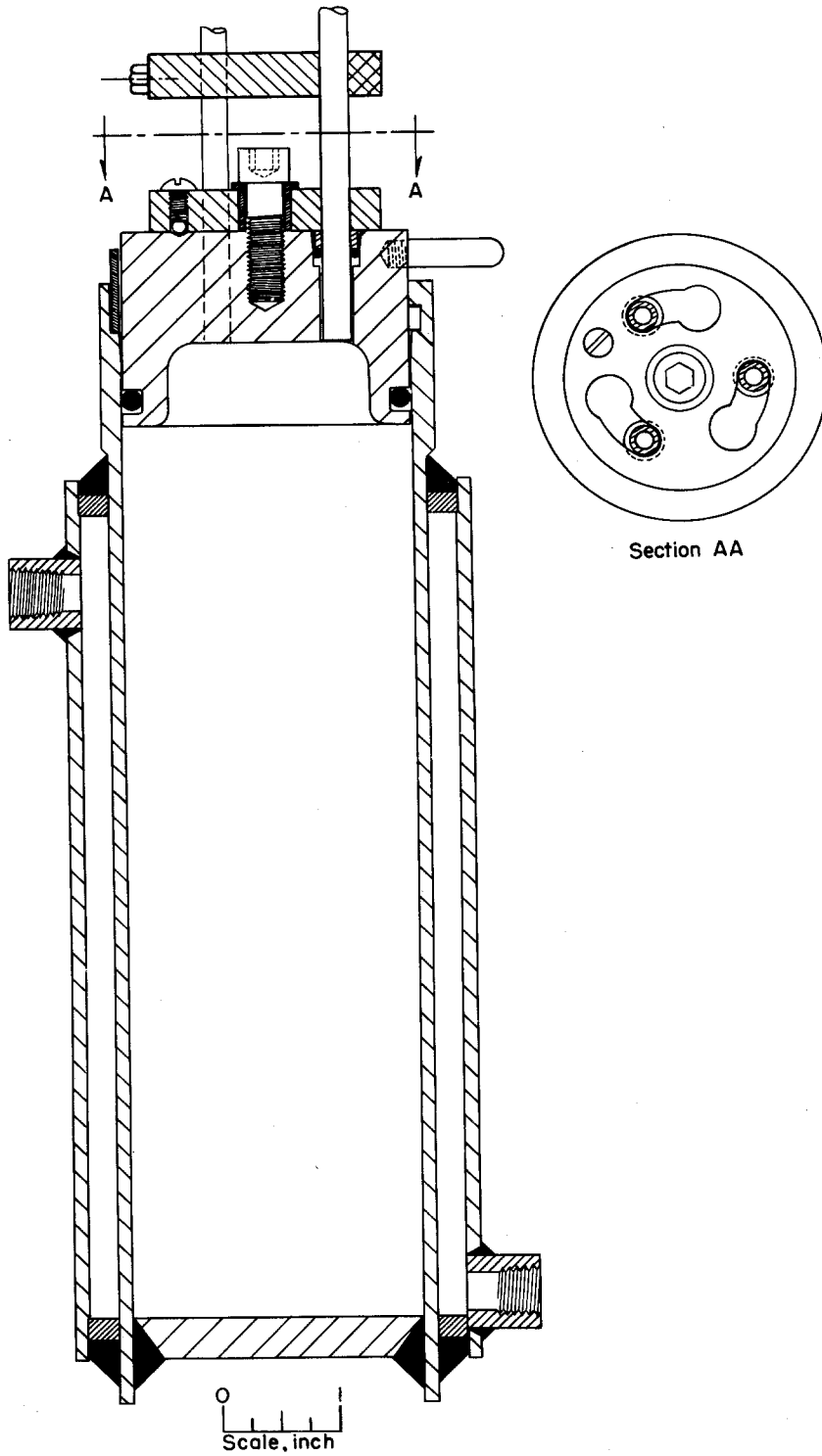


Figure 41. - Quick-opening product receiver.

A warning system is therefore incorporated in the instrument to notify operators if such a deviation should occur.

This controller has been used in 11 operations, which lasted 1 to 4 weeks. It has given completely satisfactory and trouble-free service. At no time was any pressure variation large enough to be registered on the reactor gage. If necessary, the instrument could be modified to give continuous rather than intermittent flow, which is satisfactory for the present application.

High-Pressure Flow-Meter Assembly

For metering extremely low gas flows - say, 10 to 100 cc. per hr. (S.T.P.) at pressures of at least 2,000 p.s.i.g. - an orifice is impractical because of the necessarily microscopic diameter, and a capillary element would have excessive length. This problem was solved by measuring the pressure drop across sintered disks of stainless steel 1/16 inch thick and having a pore size of 5 microns. (This material is available to 1/4 inch in thickness and 5 to 60 microns in pore sizes.) These restrictions were silver-brazed to the ends of short lengths (about 4-1/2 inches) of 1/4-inch O.D., 1/8-inch I.D. stainless-steel tubing. The tubes were fitted into high-pressure tees and installed between pressure gages. Pressure drops were varied between 50 and 200 p.s.i. at 2,000 p.s.i.g., and the exit gas (oxygen) was collected in graduated cylinders by water displacement. Tests showed that it was necessary to cover about 70 percent of the areas of the disks by silver brazing.

The final element required a 100-p.s.i. drop at 2,000 p.s.i.g. for an oxygen flow of 10 cc per hr. (S.T.P.). The accuracy of the unit is only about \pm 15 percent, but it affords a fair indication of flow rates. Minute solid particles in the gas stream probably cause the large fluctuation. A filter of the same material but having a larger area will therefore be installed upstream from the element to clean the gas.

Quick-Opening Product Receiver

In several of the units, material is emptied periodically from the product separators (at operating pressure) into product receivers (normally at atmospheric pressure). These receivers must be connected to an exit-gas meter and usually also to a source of nitrogen or other inert gas. Since a unit may be operating continuously, receivers may be emptied many times in the course of a run, and a quick-opening closure is desirable. As the contents of a unit may be toxic or irritating and as material balances are desired, accidental losses must be avoided, and the receiver must be sturdy. The vessel shown in figure 41 uses O-rings to provide a quick-opening closure. It is rated at 500-p.s.i.g. pressure at room temperature and actually withstands 750 p.s.i.g. of hydrostatic pressure.

The head of the vessel has six lugs that engage six lugs machined into the vessel wall. The head is inserted and turned 30°, engaging the projections on the head and in the vessel wall. Just below the projections on the vessel wall, the wall is machined to a taper which compresses the O-ring in the groove on the head, thus sealing the closure when the lugs are engaged. Insertion of a locking block prevents accidental turning of the head to the disengaged position. Three tubes may be inserted in the head, each being sealed with O-rings and held in place with the tube lock, which is provided with three keyhole-shaped openings for inserting and locking the tubes. All parts in contact with the product and the jacket are of type 304 or 303 stainless steel, except the O-rings. The closure works with ease and certainty.

Technical Publications

With publication of Part III of Bureau of Mines Bulletin 485, Bibliography of Pressure Hydrogenation (of coal), has been completed. A similar, two-part Bibliography of Fischer-Tropsch and Related Processes is being prepared. Compilation of the index to the literature part is nearly completed, and the patent part has been assembled and typed.

Reviews of the current status of fluid dynamics, fluid flow, the oxo synthesis, the synthesis of alcohols, early Japanese Fischer-Tropsch work, and current problems in the Fischer-Tropsch, coal-hydrogenation, and shale-oil-extraction processes have been presented in various journals and Government publications.