temperature magnetic anomaly of magnetite. Discontinuities appear on the resultant curve wherever a phase loses its ferromagnetism (the Curie point). As the shape of a thermomagnetic curve of a pure, magnetically saturated ferromagnetic substance is characteristically invariant and as its specific magnetization at saturation at any temperature and its Curie point are characteristic constants, it is theoretically possible to resolve any thermomagnetic curve into its components by characterizing these components by their Curie points (and hence to identify the corresponding ferromagnetic phases), and to determine their relative abundance by their respective contributions to the total magnetic moment.

The ideal conditions under which a curve, such as figure 79, is possible virtually never are obtained in practice. Even if saturation of all phases can be attained by using a high enough field strength, Curie points usually appear as points of inflection rather than discontinuities, and reactions may introduce spurious kinetic effects. Artifacts can also be introduced by differences in the percentage of saturation magnetization achieved because of differences in permeability between temperatures where the specimen is not fully saturated. A typical family of calculated curves, such as might be obtained with used iron Fischer-Tropsch catalysts, is shown in figure 80. This figure was constructed from actual thermomagnetic curves obtained with the pure phases. In each instance, Hägg carbide amounts to 50 percent of the ferromagnetic components, the remainder consisting of various proportions of magnetite and free iron. Obviously, the contribution of Hägg carbide to the total magnetic moment becomes insignificant not at its Curie points (247° C.) but only at about 330° C. The relative amounts of iron and magnetite in used catalysts can seldom be estimated by magnetic means because of the metastability and reactivity of these catalysts at higher temperatures. However, X-ray analysis can provide the ratio of iron to magnetite; and curves, such as those shown in figure 80, can then be resolved into their components. X-ray diffraction analysis is suitable for this estimation, because the patterns of iron and magnetite are simple and intense, owing to the high symmetry and relatively small lattice parameters of these substances. This simplicity does not exist in Hägg carbide and in cementite.

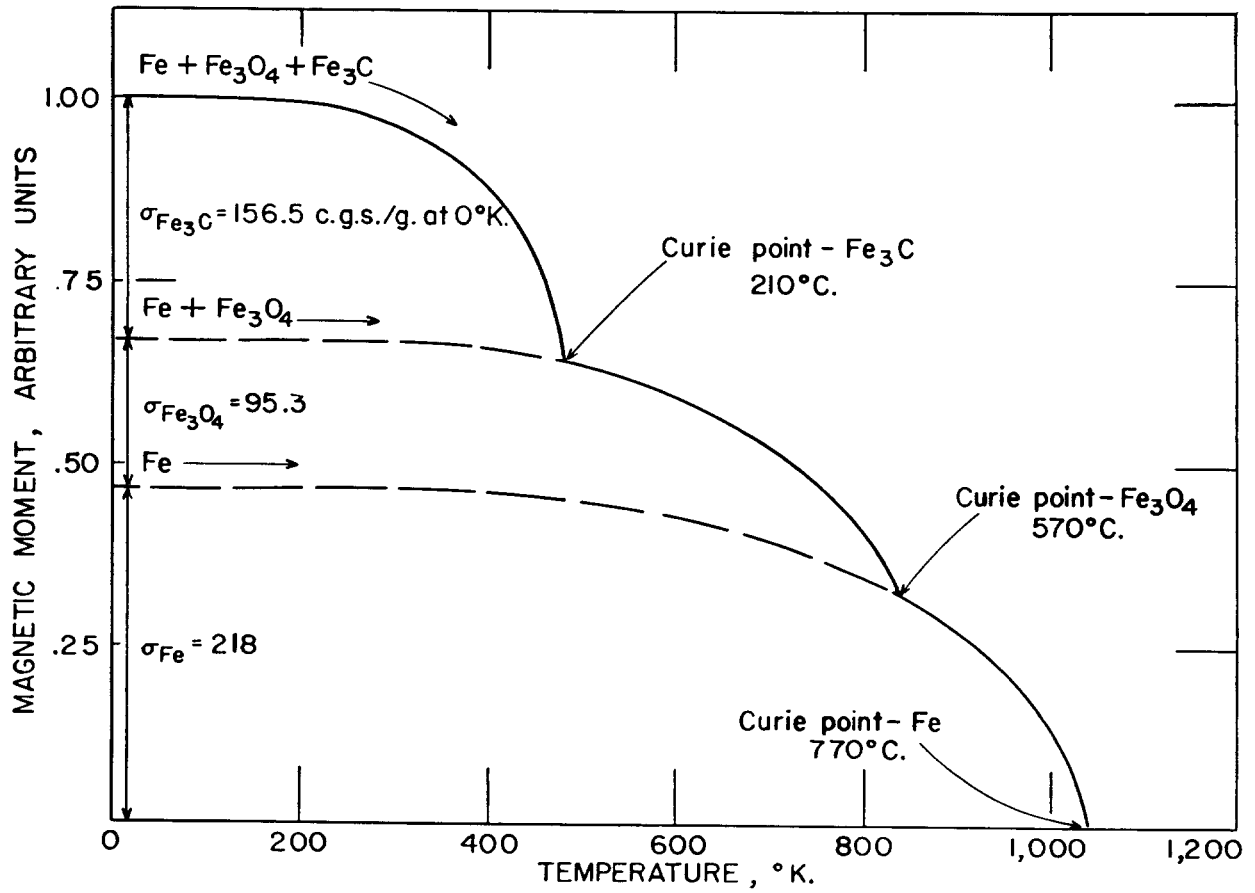

FIGURE 79.—Ideal Thermomagnetic Curve of a Mixture of Equal Amounts of α–Fe, Fe_3O_4, and Fe_3C.

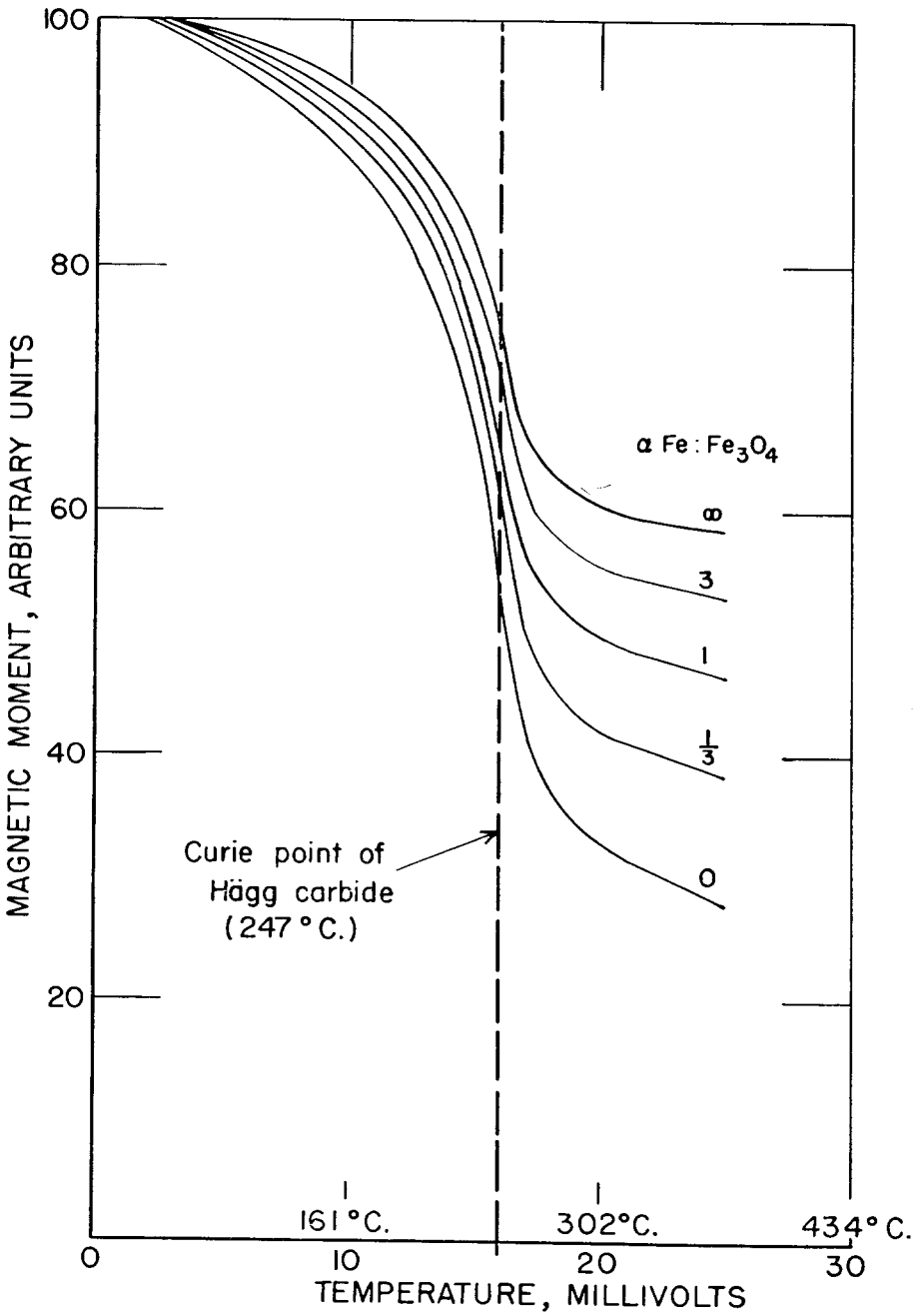

FIGURE 80.—Calculated Thermomagnetic Curves for Mixtures of α–Fe, Fe_3O_4, and Hägg-Fe_2C (50 Percent Hägg-Fe_2C).

When the sensitivity of the magnetic balance is known—that is, movement of balance beam per unit of specific magnetization—it is possible to calculate the mass of iron in each phase (assuming saturation) and thus the magnetically measured total mass of iron in a catalyst sample. If this mass is the same as that found directly by chemical determination following thermomagnetic analysis, the ferromagnetic phases in the catalyst are saturated, and all the iron can be accounted for magnetically. If, however, the magnetically determined mass of iron is less than that found chemically, the difference represents magnetically nondetectable iron. Its existence may be due to the general magnetic hardness of the sample (low permeability), small crystallite size, unfavorable crystallite shape, unfavorable crystallite orientation, type of magnetic anisotropy of the crystal, strains, nonferromagnetic inclusions, etc. For example, crystallites too small to be magnetized may be formed during phase

changes at temperatures that are too low to permit coalescence into large crystallites. Thus, carburization of iron at comparatively low temperatures may lead to the formation of small, nonsaturable, or even paramagnetic crystallites of either or both higher iron carbides simultaneously, leaving similar small, unreacted crystallites of iron. As there is an intermediate range of sizes between nonferromagnetic crystallites and those in which saturation magnetization can be attained, the apparent amounts of detectable and nondetectable ferromagnetic constituents may vary to some extent with the field strengths employed. The density of packing also affects the degree of saturation and similarly introduces discrepancies. Nevertheless, such discrepancies between the magnetically and chemically measured amounts of iron in used catalysts are of interest because of the possibility of a relationship between them and catalytic activity. A combination of magnetic, X-ray, and chemical analyses yields more complete information about used iron Fischer-Tropsch catalysts than can be obtained by using any 1 or 2 of these methods.

A special technique is employed for magnetic determination of the simultaneous presence of Hägg carbide and cementite when both are present in the same preparation. Since the Curie points of these phases (about 210° and 247° C., respectively) are close together, the heating (or cooling) must be slow, and the magnetic moments must be measured at small temperature intervals to resolve the two points of inflection. Using a relatively low field strength accentuates the changes in magnetic moments. Thus, the samples may be heated (or cooled) in a field of about 550 gauss and their magnetic moments determined at 7° C. intervals between 187° and 258° C. This type of analysis is only qualitative at present, since no method has been developed as yet to deal quantitatively with phases so far from magnetic saturation.

FERROMAGNETIC MEASUREMENT OF REACTIONS IN SOLIDS[43]

It is possible, under certain circumstances, to follow quantitatively the course of an isothermal reaction in the solid phase by observing the change of the force exerted by a magnetic field on a sample that undergoes a simultaneous chemical and ferromagnetic change. This continuous physical analysis is especially useful when a paramagnetic substance is converted to a ferromagnetic one, or vice versa. If the reaction temperature is higher than the Curie point, a phase that is ferromagnetic at room temperature becomes nonferromagnetic and has a negligible specific magnetization. It is sometimes possible to choose the reaction temperatures so that only 1 of 2 or more ferromagnetic phases is at a temperature lower than its Curie point. Similarly, if only one ferromagnetic phase is present, the reaction temperatures must not only be below its Curie point but also far enough below it so that the specific magnetization is large enough for convenient measurements. Although the specific magnetization may vary considerably over the temperature range investigated, no temperature correction need be made in correlating sets of isothermal measurements, since the amount of ferromagnetic phase present at any temperature is proportional to its magnetic moment, and since its specific magnetization remains invariant at that temperature, it is possible to express the measured force directly as the fraction (or percent) of ferromagnetic phase present.

In the simplest case a ferromagnetic substance is converted into a nonferromagnetic one, or vice versa. As a first approximation the measured force is proportional to the amount of ferromagnetic phase present in a constant magnetic field of constant field gradient. When one ferromagnetic phase is transformed into another having a different specific magnetization, the magnetic contribution of each phase must be calculated. The method is less accurate the more nearly equal the specific magnetizations of the two phases are. As the number of ferromagnetic phases present during a reaction increases, interpretation of the data becomes much more difficult.

With the equipment here described magnetic saturation is not possible because the field is too low. The force experienced by the specimen in the magnetic field may be only 60 percent of the force that would be expected if the specimen were saturated. This results from the low permeability of these specimens. By assuming that all phases are equally far from saturation, one can determine the ratio of the phases to each other. Such analyses seem to be rather good, and they may be trusted to show the growth or decline of various ferromagnetic phases in the course of a catalyst life study. In effect, however, this method ignores a large fraction of the ferromagnetic material, and if the phases reach saturation at different field strengths very sizable errors can be introduced.

Because ferromagnetism is a cooperative effect, due to interaction of a group of atoms, there is a minimum size of crystallite or particle size below which ferromagnetism is not possible. This minimum size of a ferromagnetic particle

[43] Hofer, L. J. E., Cohn, E. M., and Peebles, W. C., Isothermal Decomposition of the Carbide in a Carburized Cobalt Fischer-Tropsch Catalyst: Jour. Phys. and Colloid Chem., vol. 53, 1949, pp. 661–669.

has been determined to be 10 to 12 A. for iron [44] and about 30 to 40 A. for γ–Fe_2O_3.[45] As the ferromagnetic particles grow larger than the critical size, the specific magnetization at high fields reaches a constant value when the sample becomes magnetically saturated. This is yet another reason why the actual amount of ferromagnetic phase present at any time during the reaction may be somewhat greater than that which is calculated from the measured magnetic moment and from the specific magnetization. These discrepancies cannot be corrected, because no means are available so far for estimating the amount of ferromagnetic substance present in aggregates of subdomain size and the amount and size distribution of particles in which the magnetization is not yet fully developed.

If solid solutions are involved in a reaction, the Curie point and the specific magnetization of the ferromagnetic phase may change continuously, and a quantitative interpretation of the data may become impossible without auxiliary data.

LOADING DEVICE FOR EXTRUDING SAMPLES FOR X-RAY DIFFRACTION ANALYSIS [46]

This device (fig. 81) was designed for preparing cylindrical specimens of organic compounds suitable for use in the Debye Scherrer camera without the use of a binder. It consists of a tiny funnel just large enough to accommodate the amount of sample necessary to produce a specimen and a holding device that keeps the specimen tube properly positioned with respect to the funnel. By means of a plunger wire fastened in a small pin vise, the sample material is pushed into the specimen tube with constant tamping to consolidate the specimen uniformly throughout its length. The plunger should be a stiff No. 22 steel wire (piano wire has the requisite stiffness). The specimen tubes are 19-gage stainless steel tubing cut to the proper length (available from the Superior Tube Co., Norristown, Pa.). When the specimen tube is filled to the proper depth (about 4 mm.), the loading device is disassembled, and the specimen is extruded from the specimen-tube with the plunger wire. The plunger wire should protrude from the pin vise a distance approximately 1 mm. short of the specimen-tube length, so that the specimen cannot be completely extruded from the tube, which serves as a handle for it. Specimens produced in this way contain no binder and are strong enough to permit mounting in typical Debye-Scherrer cameras.

The neck prevents the specimen tube from being pulled out of the loading device during tamping. The anvil rod acts as a spacer and keeps the specimen tube against the neck. By using anvil rods of different lengths specimen tubes of different lengths can be accommodated. The relation between the thickness of the funnel block and the length of the specimen tube should be such that the specimen tube projects out of the funnel block, even when it has made contact with the neck. The apparatus, except for the alinement pins and the studs, is made of brass.

Pyrophoric specimens of Fischer-Tropsch catalysts were stored under petroleum ether. To prepare an extruded cylindrical specimen suitable for analysis in the Debye-Scherrer camera, the catalyst was ground to fine paste under this solvent. The paste, wet with petroleum ether, was mixed with collodion and partly extruded from a 2-cm. section of 19-gage (0.7 mm. I. D.) stainless steel tubing.[47] Such specimens were stable to the atmosphere over long periods of time. No oxidation was detectable by X-ray diffraction.

PREPARATION OF SAMPLES FOR ELECTRON MICROSCOPE [48 49]

An electron microscope has been used for examining granular catalysts. The particles were gently crushed in an effort to cause separation into ultimate particles or crystallites without altering the structure of these particles too seriously.

The crushed samples were prepared for electron-microscopic examination by two methods:

1. A supporting film was obtained by dipping a microscope slide into a 0.5-percent solution of Parlodion in amyl acetate (or Formvar in dioxane) and allowing the solvent to evaporate. The powdered sample was dusted onto the film and dispersed by exposure to a spark discharge from a high-voltage, high-frequency Tesla coil. The film was then cut into 0.25-inch squares and floated off onto a water surface. A square of film was picked up, supported on a disk of 200-mesh screen, and placed on the specimen holder of the microscope.

2. The powder was mixed with 2 drops of a 2-percent Parlodion solution and thoroughly dispersed on a microscope slide with a glass rod, amyl acetate being added during the dispersing process. A little of the suspension adhering to the rod was drawn out over a clean slide; after evaporation of the solvent, the film

[44] König, H., [The Smallest Ferromagnetic Elementary Size of Iron]: Naturwissenschaften, vol. 33, 1946, pp. 71–75.
[45] Haul, R. and Schoon, T., [Elementary Range of Ferromagnetism]: Ztschr. Elektrochem., vol. 45, 1939, pp. 663–671.
[46] Hofer, L. J. E., Peebles, W. C., and Guest, P. G., Preparing Extruded Specimens for X-Ray Diffraction Analysis: Anal. Chem., vol. 22, 1950, pp. 1218–1219.
[47] Work cited in footnote 39, p. 129.
[48] McCartney, J. T., Seligman, B., Hall, W. K., and Anderson, R. B., An Electron-Microscopic Study of Metal Oxides and Metal Oxide Catalysts: Jour. Phys. and Colloid Chem., vol. 54, 1950, pp. 505–519.
[49] Anderson, R. B., McCartney, J. T., Hall, W. K., and Hofer, L. J. E., Kieselguhrs. Suitability as Carriers in Catalysts: Ind. Eng. Chem., vol. 39, 1947, pp. 1618–1628.

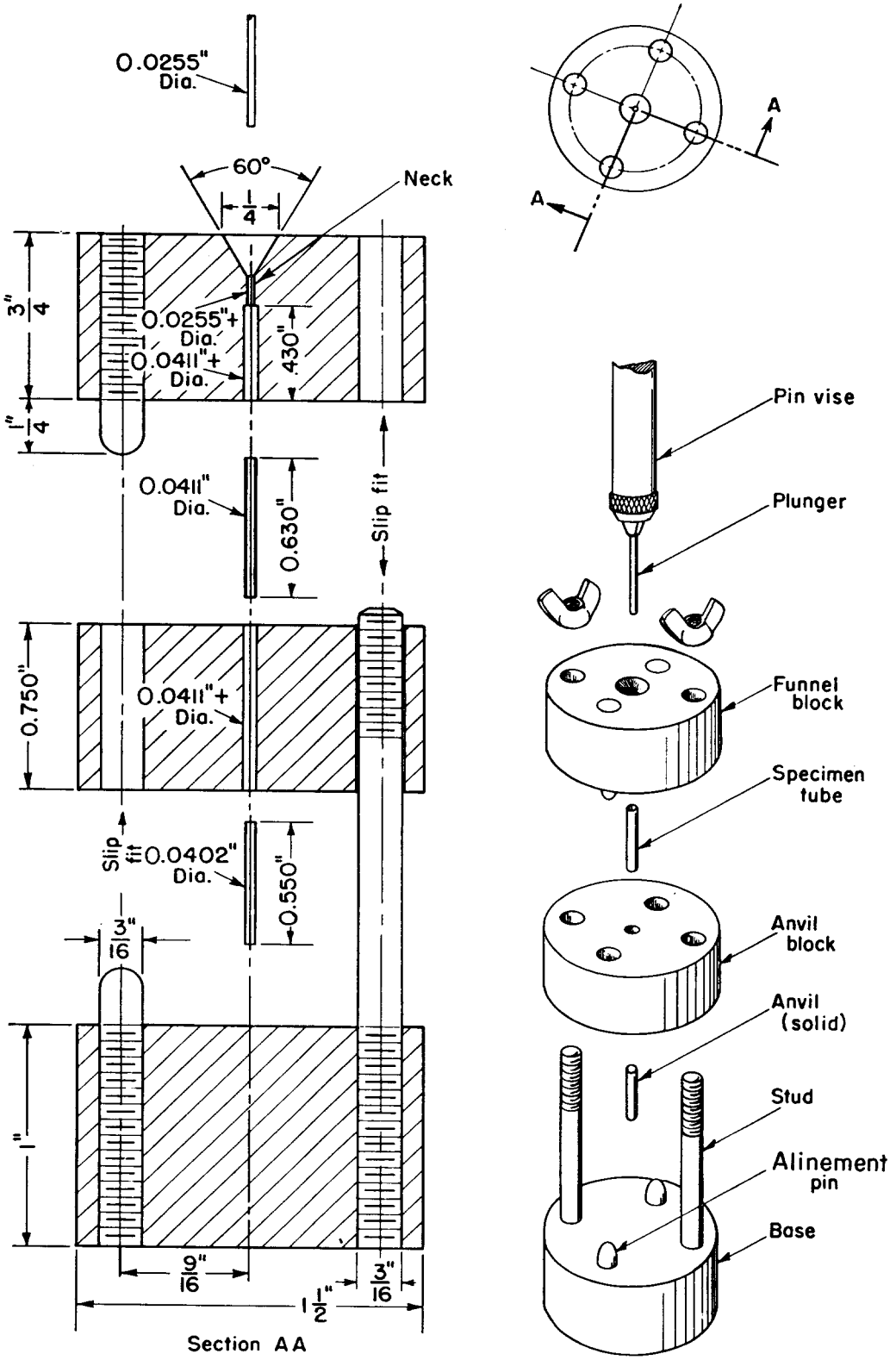

FIGURE 81.—Loading Device for Preparing Extruded Samples for X-ray Diffraction Analysis.

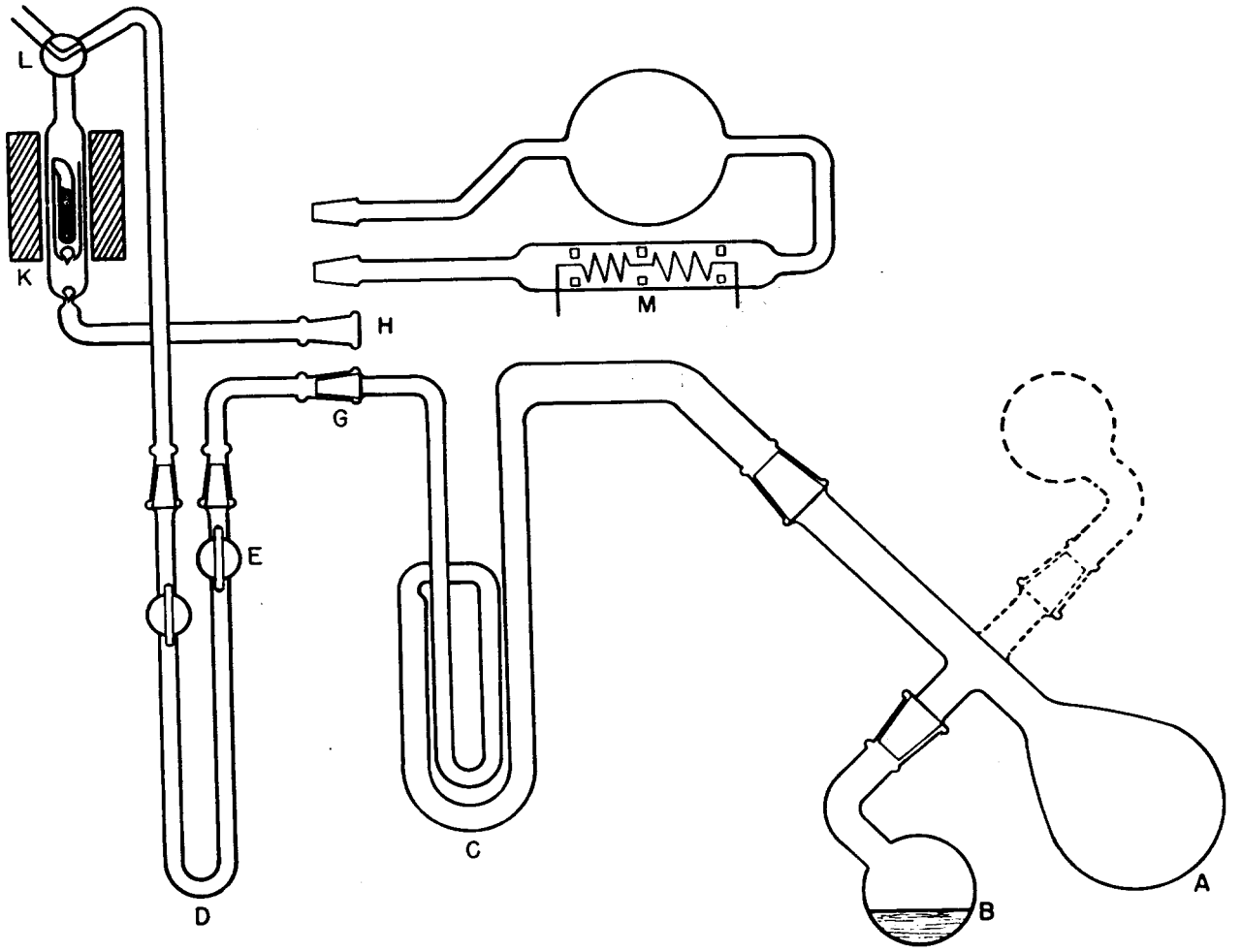

FIGURE 82.—Apparatus for Preparing Tracer Carbon Monoxide.

was cut and floated off as before. The latter method usually produced better dispersions.

PREPARATION OF CARBON MONOXIDE ENRICHED IN C^{13} [50]

The preparation of CO enriched in $C^{13}O$ from $BaCO_3$ enriched in $BaC^{13}O_3$ presents some difficulties. It is desirable to achieve almost quantitative conversion to CO of the enriched $BaCO_3$, to prepare CO of high purity, and to avoid any further dilution of C^{13} by C^{12} during the course of the conversion. These objectives can be achieved by means of the following scheme: CO_2 is prepared from $BaCO_3$ by reaction with H_3PO_4. To the CO_2, slightly less than an equimolar amount of H_2 is added. The gas mixture is then continuously circulated, by means of a small glass pump, over a platinum coil electrically heated to 1,100°–1,200° C. Water produced by the reaction

$$CO_2+H_2\rightarrow CO+H_2O \qquad (54)$$

is frozen continuously in a trap cooled by dry ice; this permits the reaction to go essentially to completion. The small amount of residual CO_2 is frozen at the end of the experiment by substituting liquid N_2 for dry ice around the trap.

When the volume of H_2 added is 2 to 3 percent less than that of the CO_2 over-all conversions of $BaCO_3$ to CO greater than 96 percent are obtained. The purity of the CO produced is illustrated by two mass-spectroscopic analyses:

Volume-percent	Run 7*b*:	Run 8*b*:
CO	99.7	99.7
CO_2	.23	.17
H_2	.07	.13

[50] Manes, M., and Weller S., Unpublished data.

The scheme presented may be modified to produce directly H_2–CO mixtures (in which the CO is enriched in $C^{13}O$) by the use of $H_2 : CO_2$ ratios greater than 1:1.

The essential parts of the apparatus are shown in figure 82. Those parts not indicated include a gas burette, a mercury-diffusion pump, and gas-storage bulbs.

A weighed amount of $BaCO_3$ is placed in *A* and an excess of 85 percent H_3PO_4 in *B*, and the system is connected as shown. Trap *C* is cooled by dry ice-acetone. The system is evacuated through the three-way stopcock *L* and then closed at *L*, and the acid is cautiously added to the $BaCO_3$ as indicated. Application of liquid N_2 to trap *D* causes condensation of the CO_2 evolved, the reaction going quickly to completion in the resulting vacuum. Stopcock *E* is closed, and the small amount of residual air is removed by opening *L* to the pump.

The gas-generating system is then removed, and the reactor *M* is connected at *H* and *G*. After evacuation of the reactor, H_2 is admitted in such amount that the CO_2 will be in excess by several percent. The liquid N_2 on *D* is replaced by dry ice-acetone, after which the magnetically operated pump *K* is started. Stopcock *L* is turned through 120°, which permits circulation of the gas mixture through *D* and over the platinum filament in *M*, which is electrically heated to 1,100°–1,200° C. The reaction is complete within 4 hours. The filament is allowed to cool, the dry ice-acetone around *D* is replaced by liquid N_2, and the excess CO_2 is removed by circulation of the gas through *D*. The remaining gas is pure CO.

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