The effect of storage under oil on the activity and selectivity of a synthetic-ammonia-type catalyst was negligible for storage periods as long as 6 months. No difference was found between the storage qualities of crude synthetic oil (made with an iron catalyst) and of oil washed with caustic to neutralize any acid, washed with water to remove the caustic, and dried to produce a dry, neutral oil.

Cementite was prepared by four different methods, using a fused catalyst, and the effect of the method of preparation on the synthesis was investigated. Partial carburization of the iron to Hägg carbide and subsequent homogenization (cementite formation) by annealing produced the most active of these catalysts for use at 100 p.s.i.g. pressure. Direct formation of cementite by carburization with methane and annealing to cementite of a mixture of Hägg carbide and metallic iron in a used catalyst yielded catalysts of lower activity. However, the presence of magnetite in the used catalyst may have had an unfavorable effect. At 300 p.s.i.g. there was no appreciable difference in activity between cementite prepared by homogenization of a mixture of Hägg carbide and metallic iron and cementite made by "typhoon" induction (see Catalyst-Oil Slurry Process).

The activities of reduced, normally inducted, and "typhoon" inducted, precipitated catalysts were also compared. "Typhoon" induction produced a remarkably active catalyst. This enhanced activity may be due in part to increased surface resulting from mechanical disintegration of the catalyst during its induction. The production of gaseous hydrocarbons was very low.

Reaction Mechanism Studies

Catalyst Composition and Reactivity

Further studies were made of the chemical properties of iron carbides, which, while not necessarily catalysts themselves, are always formed as byproducts of the synthesis and appear to have a profound effect on the activity of iron catalysts. The rate of carburization with carbon monoxide of two widely different types of catalyst obeyed the equation

$$-d(\mathrm{Fe})/dt = k(\mathrm{Fe})^2$$

at least up to about 50 percent carbiding and at gas velocities where transport cannot be a limiting factor; here t = time, k = specific reaction-rate constant, and (Fe) = mole fraction of metallic iron remaining. This rate law permitted determination of the temperature and pressure dependence of the initial rate of carburization. The activation energies varied between 27 and 32 kg.-cal. per mole, and the exponential factors for the pressure dependence varied between 0.2 and 0.3, depending on the catalyst.

The effect of alkali on carburization of reduced iron catalysts over a range of alkali concentrations and carburization temperatures was to decrease the rate of carbide formation (at least after about 50 percent of the iron had been carburized), to increase the rate of carbon deposition (after carburization was essentially completed), and to decrease the rate of reduction

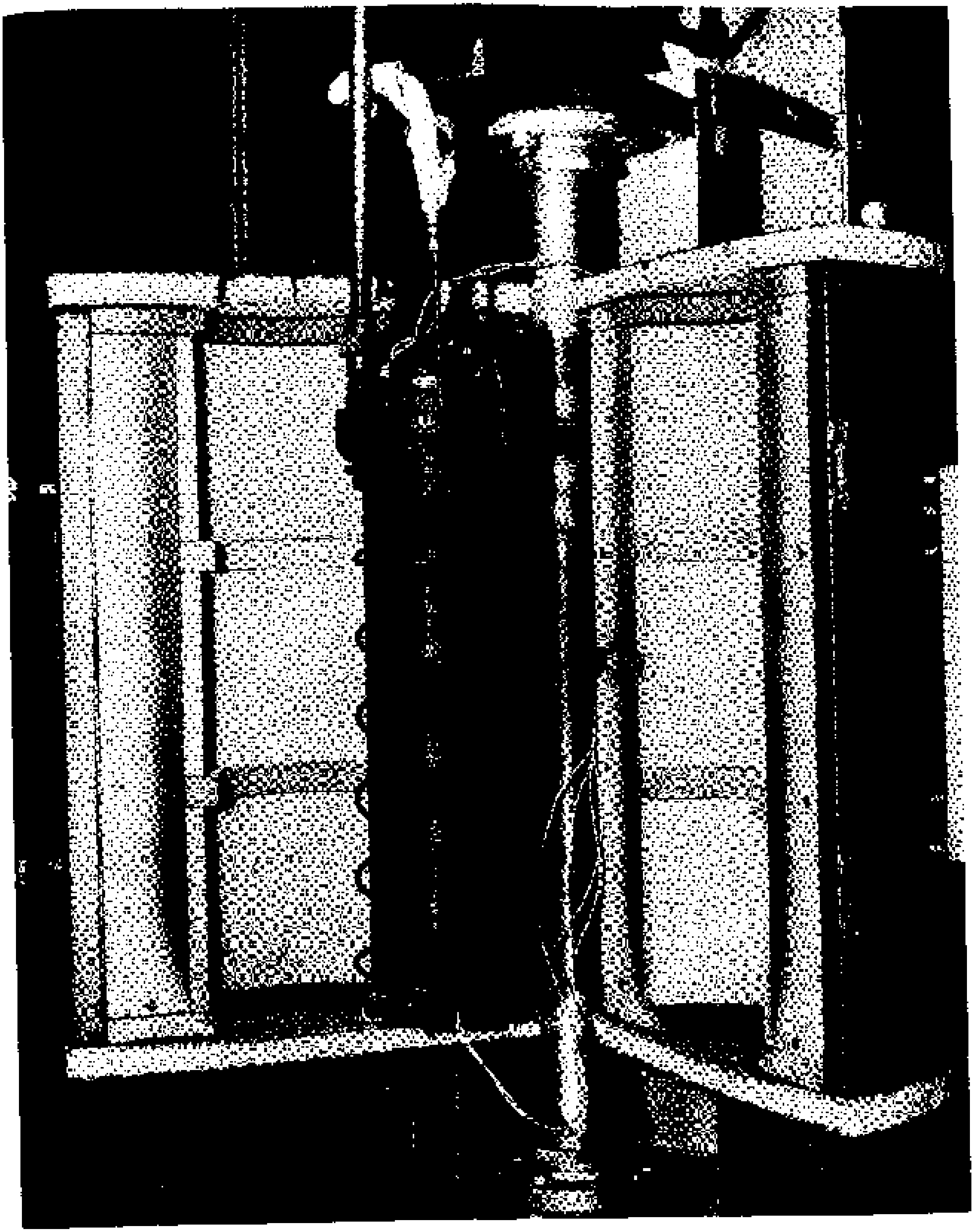

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Figure 32. - Steel-shot oxidation unit.

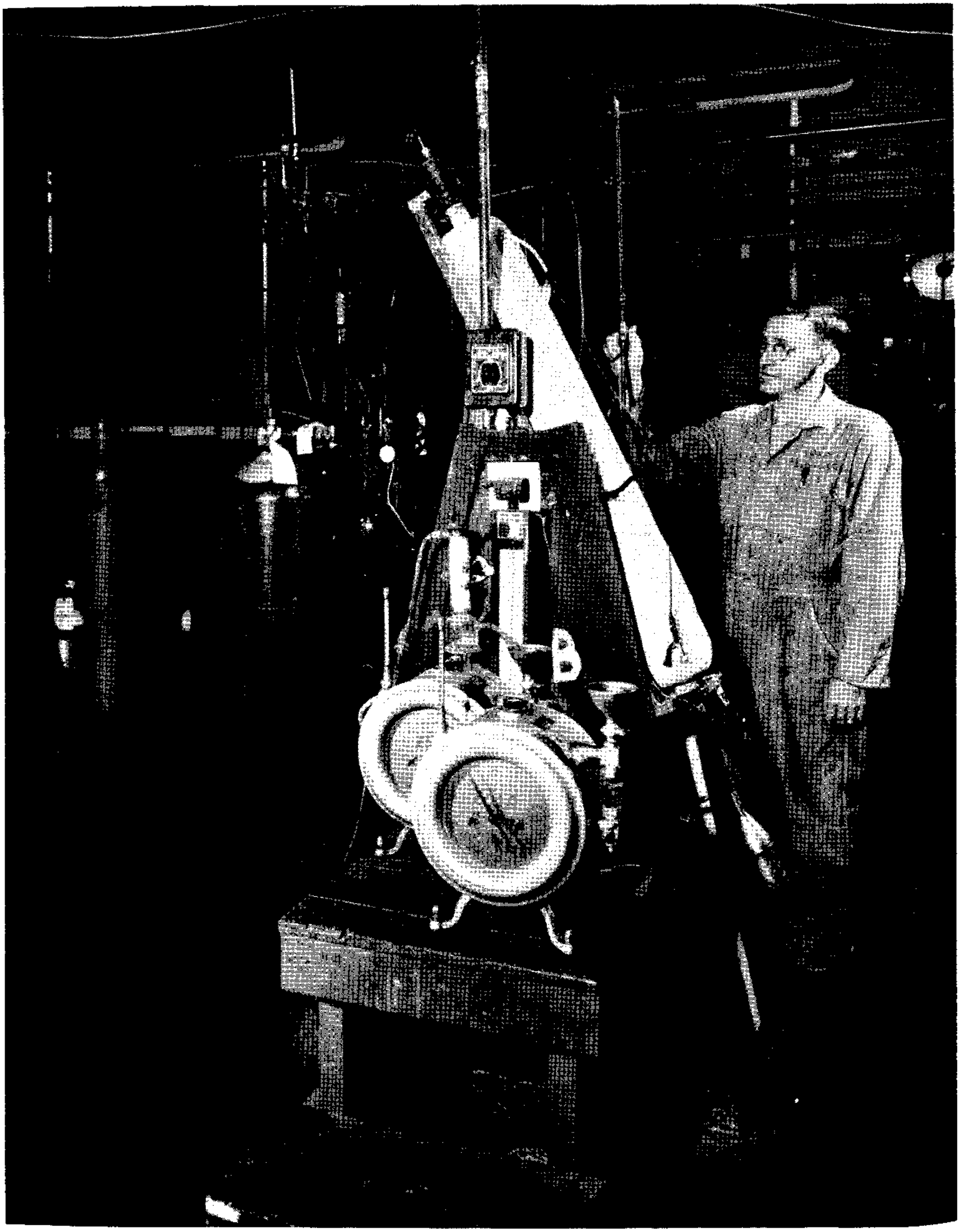

Figure 33. - Tilting reduction furnace.

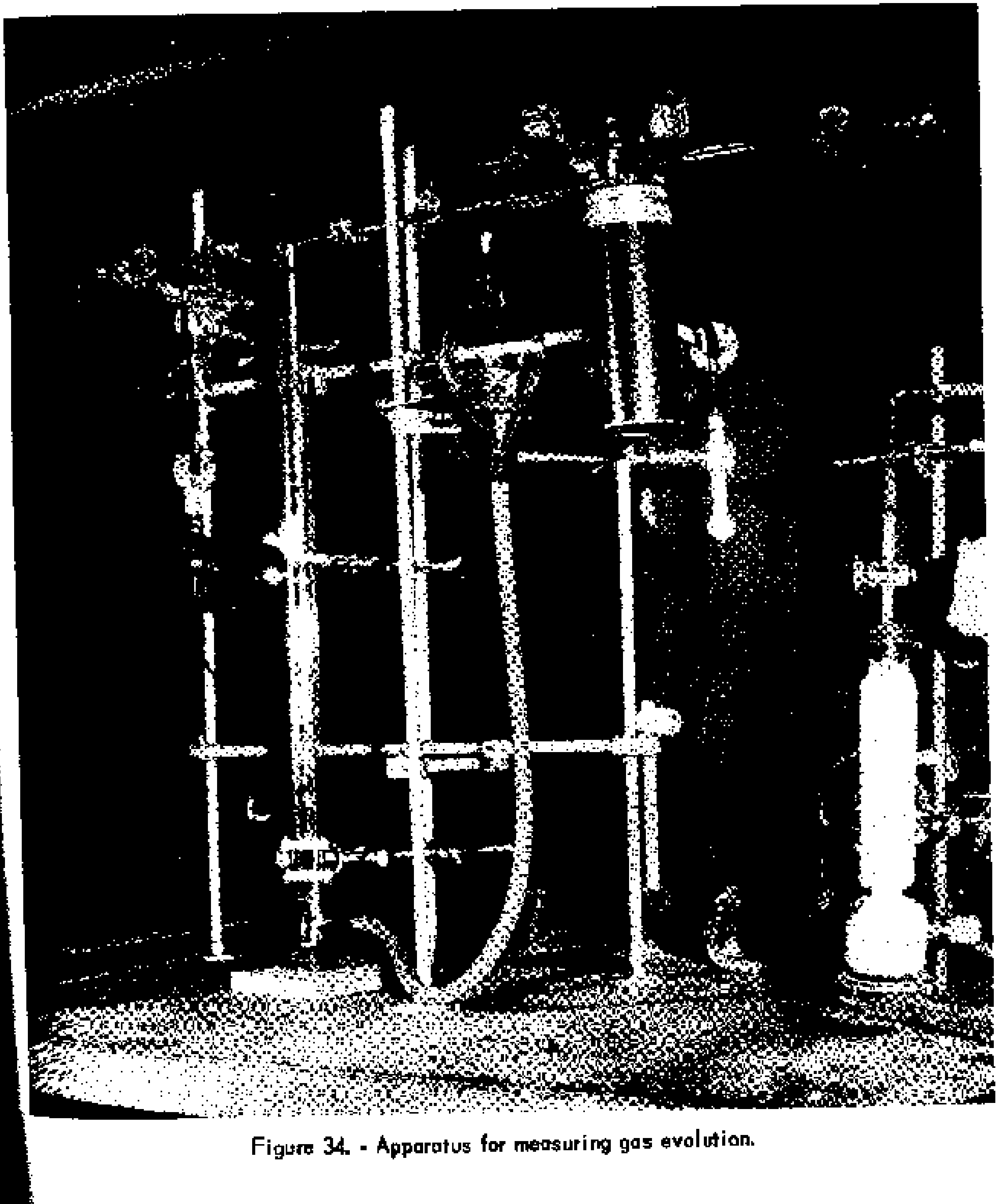

Figure 34. - Apparatus for measuring gas evolution.

Figure 35. - Glass-blowing lathe.

of the carbide. Nitriding rates of similar reduced iron catalysts were also decreased when alkali was added to the catalysts. This effect may be due to partial covering of the surface by the promoter.

Carburization of reduced catalysts with synthesis gas of varying composition was found to lead to the formation of fairly pure Hägg carbide. Although small amounts of metallic iron may remain unreacted and although formation of magnetite is increased somewhat as the ratio of hydrogen to carbon monoxide increases, the rate of carburization is rapid, and the method is simple and may be more convenient than carburization with pure carbon monoxide, especially since gas mixtures are available for the synthesis in any case.

The formation of Hägg carbide from hexagonal close-packed iron carbide was characterized magnetically by the presence of two invariant Curie points. Because Curie points are quite sensitive to changes in composition and to the formation of solid solutions, this phenomenon is proof of the fact that the transition from one structure to the other was discontinuous; that is, that nuclei of the new phase grew at the expense of the old phase, that the compositions of the two carbides remained unchanged during the transformation, and that there either was no mutual solubility of the two carbides in each other or that equilibration was too slow to become noticeable. The rearrangement proceeded without an induction period in contrast to the reaction of Hägg carbide with metallic iron to form cementite, which takes place at higher temperatures. Considering reactions of iron carbides in the solid phase, free carbon appears to be formed from carbide only by the decomposition of cementite. As this reaction occurs at temperatures far above those used in the synthesis, carbon deposition during the synthesis cannot be accounted for on this basis by thermal decomposition of iron carbide.

The reduction with hydrogen of Hägg carbide and of cementite is preceded by an induction period, after which the rates of reduction of the two carbides are essentially constant. This conclusion was reached from a study of magnetite, which was freed of alkali, reduced, and carburized - partly to form cementite (by annealing of Hägg carbide and free iron) or fully to form Hägg carbide.

One of the main causes for failure of a catalyst during synthesis is its mechanical disintegration, resulting from oxidation and simultaneous carbon deposition. To determine its susceptibility to oxidation, Hägg carbide was used in the synthesis at pressures ranging from 100 to 300 p.s.i.g. Up to an atom ratio of 0.15 of oxygen to iron, no significant effect of pressure was found on the rate of oxidation. At higher ratios, however, oxidation increased markedly with pressure. When the pressure was maintained constant and the temperature was varied between 240° and 255° C., a similar effect was observed, an increase in temperature of 15° C. being equivalent to an increase in pressure of about 50 pounds. Deposition of free carbon was rapid during the first few days of synthesis but stopped after some time.

Oxo Reaction

Reactions similar to those occurring in the oxo synthesis occur also in the Fischer-Tropsch process. In the oxo reaction, carbon monoxide and hydrogen combine with olefins or alcohols to produce oxygenated compounds of higher molecular weight than the starting materials. Cobalt usually is the catalyst, probably in the form of cobalt hydrocarbonyl, $HCo(CO)_4$, which may be formed from dicobalt octacarbonyl under synthesis conditions according to the equation

$$[Co(CO)_4]_2 + H_2 \rightleftharpoons 2HCo(CO)_4.$$

Although cobalt hydrocarbonyl can be prepared directly, it is difficult to keep as it becomes unstable above -33° C. The storage problem was partly overcome by collecting the acid in toluene and storing it in an atmosphere of carbon monoxide. Under these conditions, only very little decomposition was observed at room temperature during 24 hours (fig. 34). Methods were developed for the analysis of mixtures of cobalt carbonyl and hydrocarbonyl. A considerable amount of cobalt hydrocarbonyl was found in the reaction product from cobalt carbonate, benzene, and synthesis gas.

The formation of complexes of dicobalt octacarbonyl with organic compounds has previously been explained as a displacement of 1 or more moles of carbon monoxide by the entering organic molecule. This view has been shown to be untenable. Instead, the organic molecule effects a disproportionation of the dicobalt octacarbonyl into cobalt ion and cobalt carbonyl anion according to the generalized equation

$$2xB + 3[Co(CO)_4]_2 \rightarrow 2[Co(B)_x]^{++}[Co(CO)_4]_2^{-} + 8CO.$$

The electrons necessary for the formation of the anion may be derived from some of the cobalt or from an external source. The tendency to form the stable cobalt carbonyl anion (rare-gas structure) is probably the driving force for the reactions. Addition of electrons from an external source is illustrated by the reaction of sodium with dicobalt octacarbonyl:

$$2Na + [Co(CO)_4]_2 \rightarrow 2Na[Co(CO)_4].$$

A study is being made of the effects of contact time, temperature, catalyst concentration, and pressure on typical oxo reactions.

Characterization of Synthesis Products

Analyses

The total liquid product obtained from hydrocarbon synthesis over a nitrided-iron catalyst at 240° C. and 20 atmospheres pressure was separated into fractions by a scheme involving several distillations, extractions, and phthalation, and the fractions were analyzed by chemical and spectrographic methods (figs. 35-37). A new mass spectrometric method was developed to determine the higher alcohols in this product. The total aqueous phase represented 26.1 percent of the condensed product. Some of its components and their amounts are shown in table 15; alcohols were predominant, and ethyl alcohol was by far the largest constituent of this phase. The oil phase, 73.9 percent of the condensed product, contained more than 45 percent of oxygenates, chiefly alcohols but also significant amounts of esters. The hydrocarbons were predominantly saturated. More than 80 percent of the oil phase boiled between 50° and 350° C., and a detailed analysis of this part of the product is given in table 16.