

confirmed for concentrations of undissociated acid varying from 0.0485 molal to 7.85 molal).

The relations set forth under 3 and 4 are conveniently expressed in the general equation,

$$K_2 = (K_o' + A_o C') \frac{(\text{Cin. H}^+)}{(\text{Cin. H}^+) + (\text{Cin. H}_2^{++})}$$

which enables us to extend the application also to varying concentrations of the alkaloid.

5. The specific catalytic action of the three organic acids, formic, acetic and propionic, increases in the order of the acids named. Indeed, the absolute reaction rate for an organic acid, A_o , appears to be directly proportional to the molecular weights of the particular acids concerned—a relationship, however, which is probably accidental.

6. The specific reaction rate, which on theoretical grounds should under like conditions be independent of the initial concentration of the cinchonine or cinchonidine, is found slowly to decrease with increasing concentration of the alkaloid. In view of similar variations in rate of reaction under similar conditions in the case of such catalyses as the inversion of cane sugar and the hydrolysis of esters, these deviations from constancy in the case of the cinchona alkaloids are not to be regarded as abnormal.

7. The specific reaction rates of the two isomeric alkaloids under like conditions bear to each other a constant ratio, whose mean value is, cinchonidine to cinchonine, 1 : 1.21. This difference in rate of conversion is apparently to be attributed solely to the stereoisomeric difference existing between the two alkaloids.

8. A tentative suggestion as to the mechanism of the reaction involved in the conversion of the cinchona alkaloids into their toxins is offered on the basis of the readiness with which organic acids yield acyl derivatives with primary and secondary amines.

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AN APPARATUS FOR THE STUDY OF REACTIONS BETWEEN GASES AND LIQUIDS.

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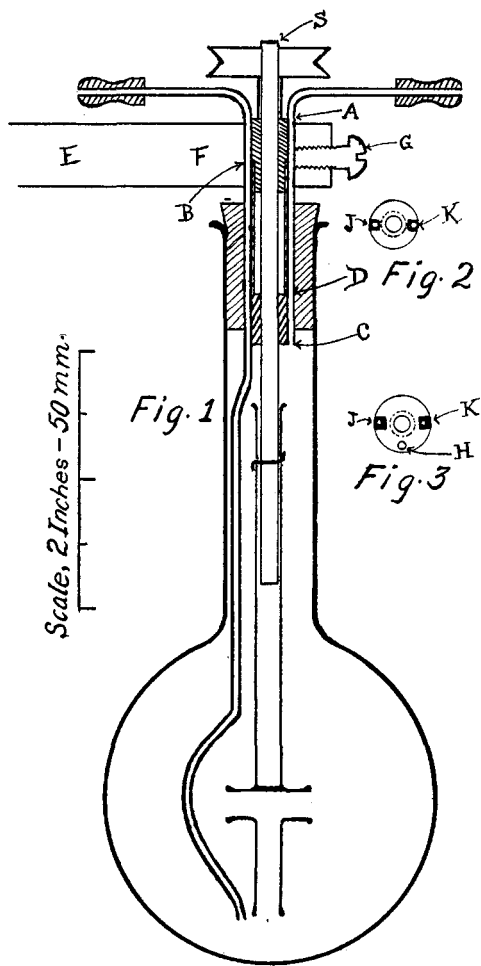
The apparatus here described has been devised and used for the study of catalytic hydrogenation, but may serve for the study of any reaction in which a gas is to be brought into intimate contact with a liquid under constant conditions. The problem is to introduce a high speed stirrer, inlet and outlet tubes, and, possibly, a sampling tube through a comparatively small stopper and to render the whole gas tight for both increased and reduced pressure. The apparatus is shown in the sketch in section, Fig. 1.

The bearing, AC, is made of two pieces of steel rod, AB, and BC, 0.5 and 1.5 inches long, respectively. Both of these have a $\frac{1}{8}$ in. hole drilled longitudinally through them, then the longer one is drilled out to a size of about $\frac{1}{32}$ for most of its length, *i. e.*, from B to D. The shorter piece is turned down for half its length till it fits closely into the other, so that a double bearing is formed, with an enlarged cavity in the central portion. The two parts are assembled and channels about $\frac{1}{16}$ by $\frac{1}{16}$ in. are cut in opposite sides as shown at J and K in cross section in Fig. 2. Care must be taken that the channels do not cut through the walls of the cavity. The $\frac{1}{16}$ brass tubes that are used for the gas inlet and outlet tubes are laid in these channels which are then filled with solder, the solder more than filling the channels. The excess of solder is turned off in the lathe so that the whole is a perfect cylinder externally and adapted to make a tight joint when passed through a cork.

The stirrer may be of any suitable form, but the Witt centrifugal stirrer shown is one of the best, as, when run at high speed, it effects very thorough mixing. The stirrer may be made of glass and fastened to the shaft by a bit of wire which

passes through a hole in the shaft and through holes in the stirrer. The shaft, S, is of $\frac{1}{8}$ in. drill rod and carries a pulley of suitable size. The inlet and outlet tubes are bent as shown and carry enlargements so as to make convenient joints with rubber tubing.

The bearing passes through a hole in a 0.5 in. rod, EF, and is held in place by a set screw, G. This rod is conveniently clamped to a laboratory iron stand.



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To assemble the apparatus, the shaft is pushed a short distance into the bearing from the bottom and mercury is poured in. The shaft is then pushed on through, causing the excess of mercury to overflow and leaving the cavity in the bearing filled with mercury. Thus a gastight mercury seal is formed which is tight no matter how fast the shaft rotates. To make a stuffing box gastight would require so much pressure that the rotation of the shaft would be hindered. The mercury seal, though tight, offers no resistance to the motion of the shaft. This seal is tight against either excess or diminished pressure for moderate pressures. The apparatus in use proved to be gastight under a pressure of 3 feet of water. The shaft must fit the bearings very accurately to avoid danger of loss of mercury, but little trouble has been met with in this respect. Lubrication is accomplished by placing a drop of oil above and below the bearings and working the shaft up and down a few times. This should be done each time the apparatus is used.

In case it is desired to take out samples during the course of the reaction, the bearing is cut from somewhat larger rod and a hole is drilled through the assembled bearing, to one side, as shown in section at H in Fig. 3. This hole is stopped by a plug lubricated with oil. For taking out a sample, a piece of 0.25 in. glass tubing is drawn out to a capillary about 6 in. long. This is passed down through the hole in the bearing and the desired amount of liquid drawn out. A hole is drilled in the web of the pulley so that it can be brought over the hole in the bearing and allow the capillary to pass. In studying the velocity of the reaction, the time is taken till the moment that the stirrer is stopped. Taking out a sample requires about one minute. The time for the next period is taken from the moment that the stirrer is again started. Experiments have shown that reactions of this sort, depending on stirring, stand practically still when the stirrer is not in operation.

The size apparatus here described has proved extremely useful for small scale work of a variety of kinds. Obviously, the same plan might be used for apparatus for larger operations. The flask is heated to any desired temperature by being placed in a suitable bath. Temperatures up to 220° have been used. The stirrer has been run by an electric motor, a rubber band serving as a convenient belt. Speeds of 3000 to 4400 revolutions per minute have been obtained without difficulty.

One application of this apparatus will be described in the following communication. It is here described in the hope that it may be of service to those who are working on reactions involving gases and liquids.