AN APPARATUS FOR MICRO-CATALYTIC HYDROGENATION

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In the course of some work concerning the reduction of chlorophyll derivatives,[1] it became necessary to have a means of quantitatively measuring the amounts of gas absorbed by very small samples of material. The most desirable form of apparatus seemed to be either that devised by Barcroft,[2] or that devised by Warburg.[3] Both forms are used extensively by biologists for measuring reactions which involve small quantities of gases

After a modified form of the Barcroft apparatus had been used with moderate success, the apparatus to be described was devised. It seems to be better adapted for chemical purposes than either of the other types mentioned, since it is equally accurate and is more easily manipulated. It is furthermore much less expensive than the present form of the Warburg apparatus.

The details of construction of the apparatus are shown in Fig. 1. It is most easily made from pyrex glass. The dimensions may be varied depending upon the size of samples with which one expects to be working. For reactions involving quantities of gas up to 0.04 millimole, the following size was found to be convenient. The bottles, A and A₁, are of sixty to seventy cubic centimeters' capacity. The manometer side arms are twenty centimeters in length and are made from one millimeter capillary tubing. The three way stopcock at E allows repeated evacuation and filling of the apparatus with the de-

Fig 1.

sired gas. The stopcock at D holds back the manometer liquid during evacuation and filling. The section of medium-sized glass tubing between F and D acts as a reservoir for the manometer liquid. F consists of a rubber tube closed at the upper end by a glass rod, and is fitted with a screw-clamp,
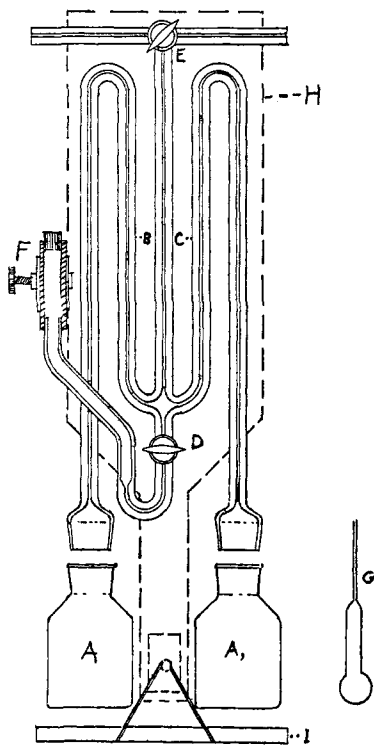
[1] Conant and Hyde, THIS JOURNAL, 52, 1233 (1930).

[2] Barcroft and Haldane, J. Physiol., 28, 233 (1902).

[3] Warburg, Biochem. Z., 152, 51–63 (1924).

by means of which the liquid can be drained from the manometer or set at any level as in the Warburg apparatus. This arrangement makes it possible to take readings very rapidly. The glass apparatus is fastened to the wooden mounting H with a millimeter scale attached along the middle capillary tube. F is conveniently attached to either side of the mounting. The bottles A and A_1 are held in position by means of a small block of wood, I, which is placed under the bottles and held there firmly by passing under it a rubber band or wire spring, the ends of which are fastened to the wooden mounting. The latter is provided with a bearing near the center, by which it is supported on a shaft whose axis is perpendicular to the plane of the apparatus. Shaking is accomplished by means of a connecting arm attached to the mounting at a position near the top. The other end of the arm is fastened to a motor-driven eccentric. The shaft carrying the apparatus is clamped to a ringstand in such a way that it can be raised and lowered easily, since the bottles are to be immersed in a water-bath during the course of a reaction in order to keep both bottles at the same temperature. The sample tube G is made from ordinary six millimeter glass tubing about eight centimeters in length. A small bulb is blown on the end so that the glass is comparatively thin and can be broken at the proper time by shaking. With a little practice they are easily made so that premature breaking from the shaking of the apparatus at its usual speed (300–400 vibrations per minute) is avoided. The breaking of the tube at the desired time is made easier by inserting along with the sample a short pointed piece of glass rod. Before mounting the glass part it is necessary to measure as accurately as possible the volume in each side of the apparatus, including the bottles and the capillary up to the positions marked B and C in the manometer arms. This permits using the proper amounts of solvent in each bottle to make the remaining gas volumes equal to each other. The volume measurement is accomplished by filling with mercury and weighing.

The principle is the same as that involved in the use of the Warburg apparatus, namely, measuring the change in pressure at constant volume. The difference in pressure in the bottles A and A_1 is obtained by raising the level of the manometer liquid to the positions marked B and C successively, and each time noting the position of the meniscus in the central capillary tube. If these respective heights are designated h_B and h_C, the difference between the initial value of $h_B - h_C$ and the final value of h^1_B and h^1_C, after equilibrium has been established in the reaction, becomes a measure of the pressure change due to absorption of gas during the reaction. Since the filling in both sides of the apparatus is the same except for the sample, the one side serves as a blank.

The readings obtained as described are independent of any partial pressure effects, of the initial pressure, and of changes in atmospheric pressure. This can be shown in the following way. Let P and P_1 be the

initial and final pressures, respectively, in a reaction involving n_C moles of gas. Suppose that the initial pressure had been P_2 instead, with the corresponding final pressure P_3. Since the temperature is assumed constant, we may write the following equation from the gas law,

$$\frac{P}{n} = \frac{P_1}{n_1} = \frac{P_2}{n_2} = \frac{P_3}{n_3} \tag{1}$$

where n, n_1, n_2, n_3 are the corresponding number of moles of gas present in the given volume.

Then

$$\frac{P - P_1}{n - n_1} = \frac{P_1}{n_1} = \frac{P_3}{n_3} = \frac{P_2 - P_3}{n_2 - n_3} \tag{2}$$

but by definition

$$n - n_1 = n_2 - n_3 = n_C \tag{3}$$

hence

$$P - P_1 = P_2 - P_3$$

The reading is, however, not independent of temperature changes. A simply constructed thermostat is suitable to use in measuring rates, but under ordinary circumstances, where it is desired to know only the total amount of gas absorbed, a few degrees' change in the temperature of the water-bath is negligible. The readings can be corrected for any temperature change if it is necessary, as is shown by the following calculations. Let P and P_1 be the initial and final readings at temperature T, and let P^1 and P_1^1 be the initial and final readings at a temperature T^1. Then, considering the volume as constant, the following equations can be written

$$\frac{P}{T} = \frac{P^1}{T^1} \quad \text{and} \quad \frac{P_1}{T} = \frac{P_1^1}{T^1}$$

Subtracting the second equation from the first, the following equations are obtained

$$\frac{P - P_1}{T} = \frac{P^1 - P_1^1}{T^1}, \quad \text{or}$$

$$P - P_1 = (P^1 - P_1^1) \frac{T}{T^1} \tag{4}$$

The correction therefore involves multiplying the one reading by the ratio of the absolute temperatures.

The number of millimoles of gas equivalent to a change in pressure of one centimeter of the manometer liquid is calculated from the equation

$$n/cm = \frac{V \times 273 \times d}{T \times 22.4 \times 1033} \tag{5}$$

where V is the volume of gas, d is the density of the manometer liquid, and T is the average absolute temperature of the bath. If the same gas volume is used, n/cm will be always the same.

The substance is weighed into the sample tube, using a small glass tube as a funnel so that none of the material sticks to the part which will be heated. The sample tube is then drawn out to a thin capillary of such length and diameter that it will just about

enter the capillary tube in the stopper of the reaction bottle, but is not sealed off. The bottles A and A_1 are then filled with the proper amounts of solvent and approximately two milligrams of platinum oxide catalyst, prepared in the manner described by Adams and Shriner.[4] The sample tube is placed in one of the bottles. The bottles are then placed in position and made fast after the ground joints are lightly greased. Excess grease is avoided, since it may dissolve in the solvent or the catalyst may stick to any exposed greasy surface. The apparatus is now evacuated four or five times with the stopcock D closed, each time refilling with hydrogen. It is very convenient to have one arm of the stopcock E connected throughout the run to a large bottle, which serves as a gas reservoir. The reservoir bottle is in turn attached by a siphon tube to another bottle so that as gas is used in sweeping out and filling the apparatus, it is displaced by water. The stopcock D is turned so that the apparatus and reservoir are connected. The apparatus is shaken for two to five minutes, during which time the platinum oxide is reduced. The shaking is now interrupted and the manometer liquid raised so that readings may be taken at B and C. The apparatus is now trapped off from the reservoir by the manometer liquid. The shaking is continued until after a ten or fifteen minute period the value of $h_B - h_C$ is constant. This usually requires from half to three-quarters of an hour. At this point, if found desirable, the pressures may be readjusted by lowering the manometer liquid below the junction and raising it again. The apparatus is then removed from its shaft and the sample tube broken by a vigorous shake while holding it with the hands. With this accomplished the apparatus is replaced and the shaking continued. Readings are taken at frequent intervals until the pressure difference $h_B - h_C$ becomes constant, indicating that equilibrium is again reached. In taking readings the shaking is interrupted by seizing the apparatus with one hand and adjusting the manometer levels with the other. The belt of the motor used for shaking is therefore adjusted so that it will slip with a little added resistance without jumping off. The product of the pressure change in centimeters multiplied by the calculated number of millimoles per centimeter is the number of millimoles of gas absorbed.

Table I contains some typical results for catalytic hydrogenation which show that an accuracy of $\pm 2\%$ is readily obtainable. In all these experiments the gas volume V was 68.4 cc. The manometer liquid was tetrachloro-ethane, density 1.58, and the temperature of the bath was 298°K. The corresponding value of n/cm was 0.0043 millimole. Glacial acetic acid was used as a solvent, 5 cc. being used in each experiment. In some cases the samples were weighed on a micro balance and in others aliquot portions of a solution of a larger sample were taken. The time required for the complete reduction of these substances was between thirty and sixty minutes.

TABLE I

EXPERIMENTAL DATA

Substance	Millimoles of sample	Change of pressure, cm.	Millimoles of H_2 absorbed
Maleic acid	0.0267	6.1	0.0263
Maleic acid	.0384	9.2	.0392
Dimethylacrylic acid	.0277	6.35	.0272
Dimethylacrylic acid	.0391	9.35	.0399
d-Pinene	.0394	9.6	.041
d-Pinene	.0394	9.35	.040

[4] Adams and Shriner, THIS JOURNAL, 45, 2171 (1923).

These results indicate that any possible sources of error such as a change in the state of saturation of the catalyst with the slight change in pressure may be neglected.   In one or two instances the sample failed to be reduced, presumably on account of poisoning of the catalyst.   This difficulty was largely eliminated by washing the reaction bottle thoroughly each time, rinsing with 10% potassium hydroxide solution and finally with distilled water.

The apparatus is not limited in use to hydrogenations.   It has already been used with success in measuring the rate and extent of oxygen absorption of free radicals.   In this work,[5] it has been found that using a 5-cc. sample of 0.01 M solution of free radical in tetrachloro-ethane at 25° and shaking at the rate of 400 vibrations per minute, absorption rates of oxygen having a half-time period as low as thirty-four seconds can be measured. The rate of solution of oxygen is great enough to maintain 90% saturation in the liquid phase under the stipulated conditions.

It has been suggested to us that this apparatus might be used for the measurement of vapor tension and its depression by solutes, photochemical and catalytic accelerations, equilibria in gas reactions involving liquids, solids or other gases and in bacteriological studies, such as those concerned with nitrogen-fixing bacteria.

Summary

1.   An apparatus for the measurement of small quantities of gas absorbed or evolved in a chemical reaction has been described.

2.   It is particularly adapted to catalytic hydrogenations on a micro-scale, in which case an accuracy of ±2% has been obtained under the conditions described.

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[5] To be published by Conant and Scherp.