

A Modification of the Microhydrogenation Apparatus of Breitschneider and Burger

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For the accurate determination of the hydrogen absorption of catalytically hydrogenated organic compounds, the best methods so far developed are based on the principle shown in Fig. 1. Hydrogenation takes place in the vessel I, which communicates with a compensation vessel II by a manometer. During hydrogenation, the drop of pressure in I is compensated by the addition of mercury from a burette, and the manometer is in this way kept at zero. The amount of hydrogen h (in ml at 0°/760 mm Hg) consumed by the substance is given by equation (1)

$$h = \frac{273}{260} (B - e) \frac{a}{T} \quad (1)$$

a is the volume of added mercury in milliliter; T the absolute temperature; B the atmospheric pressure in mm Hg and e the vapour pressure of the solvent in millimeter Hg at T° .

The above principle was introduced by Smith¹, and later employed by Slotta and Blanke², Jackson and Jones³, Breitschneider and Burger⁴ and Prater and Haagen-Smit⁵. The advantage of the method as compared to other methods has been reviewed by Breitschneider and Burger (*cf.* also Pfeil⁶).

In this communication we report some modifications of the apparatus of Breitschneider and Burger. Magnetic stirring has been employed to avoid the use of the fragile glass coil which connects the hydrogenation vessel with the manometer; the air is washed out by a stream of hydrogen without evacuating the entire apparatus; this makes it possible to dispense with an arrangement to remove the manometer liquid. The new apparatus is simpler, and easier to handle, while the obtainable accuracy remains the same.

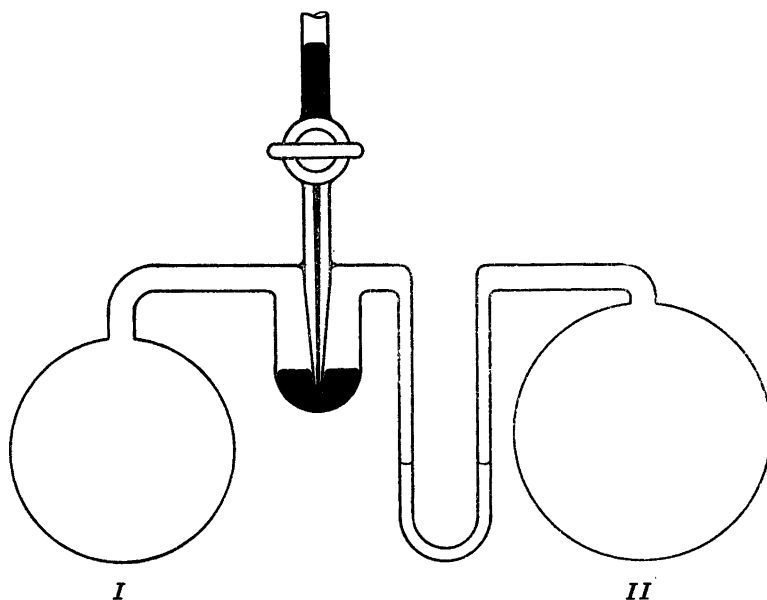


Fig. 1. Principle of the method. I hydrogenation vessel, II compensation vessel.

APPARATUS

Figure 2 gives a detailed design of the apparatus⁷. The total volume of the parts on either side of the manometer is about 70 ml and the two volumes should be of the same size within 2–3 ml.

The graduation of the manometer must not necessarily be very accurate inasmuch as it is only used to adjust the pressure difference to zero. A 2 centimeter long graduation in millimeters is very convenient.

The burette is about 40 cm long and contains 5 ml. Every milliliter is graduated in 50 parts; of course a longer and more accurate burette may equally well be employed. The tip of the burette is so fine, that one milliliter of mercury flows through it in about one minute. It is therefore not necessary to adjust the flow of mercury with the cock *b*.

p is a platinum beaker to which a 25 mm long iron rod is attached, so that the beaker may be hooked off and dropped into the solvent by means of a magnet. The rod is wrapped in a platinum sheet, soldered with gold, to avoid corrosion of the iron by the solvent.

The whole apparatus is supported by a clamp just beneath the cock *b*, and immersed into a glass disk filled with water. The water is stirred efficiently to assure equality of temperature throughout the bath. The liquid in the

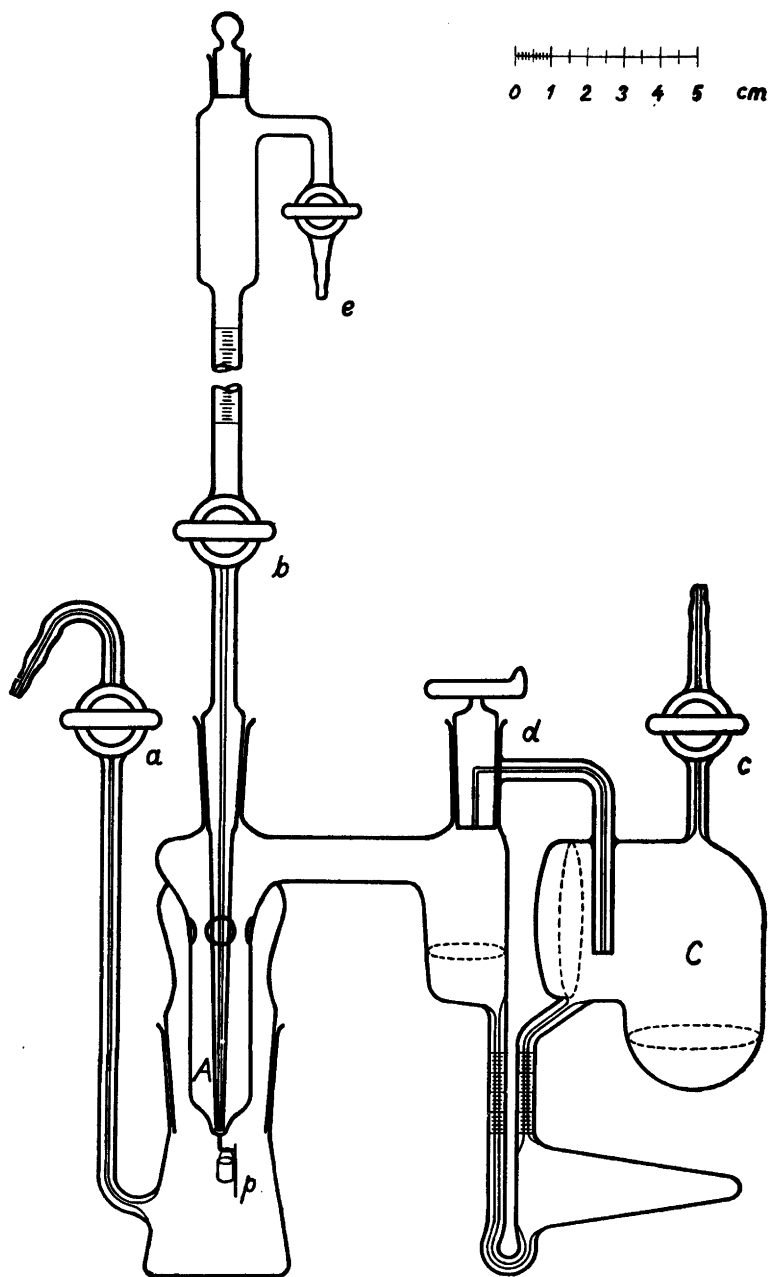


Fig. 2. Apparatus. *A* reservoir for mercury; *C* compensation vessel; *a*, *b*, *c*, *d* and *e* cocks; *p* platinum beaker.

hydrogenation vessel is agitated by a glass-jacketed rod, which is rotated by a revolving magnet placed under the glass disk.

Before use the apparatus is cleaned, and the cocks carefully greased. Mercury is filled into *A*, and sucked up into the burette by applying suction to *e*. When the mercury has reached the upper mark of the burette, *b* is closed, and suction turned off. There should now only be a small amount of mercury left in *A*, just enough to cover the tip of the end of the burette.

PROCEDURE

The solvent is filled into *C* (about 2 ml) and into the manometer. These operations are performed by disconnecting the cock *d*. Now the catalyst and 2 ml of the solvent are placed in the hydrogenation vessel. The substance to be analyzed is weighed into the platinum beaker, which eventually is suspended on the glass hook. Then the hydrogenation vessel is connected with the main part of the apparatus and the air in the whole apparatus removed by leading a stream of hydrogen through *c* with *d* and *a* open (note 1).

When all air has been removed, first *a* and, shortly after, *c* are closed. In this way the pressure inside the apparatus will become slightly higher than that of the atmosphere. Stirring is started in order to hydrogenate the catalyst. At the same time the hydrogen becomes saturated with the vapours of the solvent. When the catalyst is perfectly hydrogenated, the manometer will remain on level if *d* is closed. Now the excess pressure is relieved by opening *a* for a moment (*d* must be open). The temperature and the atmospheric pressure are registered. *d* is closed and hydrogenation commenced by dropping the beaker with the substance into the solvent.

Absorption of hydrogen causes the left part of the manometer to be filled with the manometer liquid (note 2). When a reading of the consumption of hydrogen is desired, stirring is stopped, and mercury let into *A* until the manometer again stands on level (note 3). Hydrogenation is continued till no decrease of pressure is observed and the manometer remains on level.

Note 1. For the usual precautions concerning the employed reagents etc. see the monograph of Pregl on quantitative organic microanalysis. (5th ed., Vienna 1947.)

Note 2. The volumes of the different parts of the apparatus are chosen so that 5 ml of hydrogen, that is the total content of the burette, may be consumed without causing the solvent to flow into *A*. The apparatus must thus not be attended to during hydrogenation, if only the equivalent weight of the substance is to be determined.

Note 3. Temperature fluctuations of the order of one degree may cause a small pressure difference due to volumetric changes of the solvent and the glass. If a very accurate determination is desired, the temperature of the water bath should therefore be kept constant within about 0.5°.

EXPERIMENTS

Sorbic acid ($M = 112.06$) was employed to test the apparatus. The sample was alternately sublimated in vacuum (twice) and recrystallized from water

(three times). The results of five hydrogenations in 2 ml of alcohol with Adam's catalyst are cited below.

Sample mg	PtO ₂ mg	B mm	e mm	T°	a after 90 minutes ml	a after 5, 10, 15, 20 and 40 hours, respectively	a calc.	Error %
8,931	13	771.7	38.0	273 + 17.7	3,952	3,952	3,955	0.1
8,726	10	771.2	39.6	273 + 18.4	3,882	3,883	3,885	0.1
8,583	8	773.8	42.3	273 + 19.5	3,835	3,835	3,836	0.0
8,845	5	764.4	39.0	273 + 18.1	3,961	3,961	3,967	0.1
3,451	4	764.8	38.2	273 + 17.8	1,541	1,542	1,544	0.1

The experiments demonstrate, that the error is less than 0.2 % even after hydrogenation for 40 hours.

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