NEW APPARATUS

A LOW PRESSURE HYDROGENATOR OF WIDE APPLICATION

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A number of low-pressure catalytic hydrogenators have been described in the literature, most of them being intended for use in the determination of structure, in which the hydrogen absorbed by small quantities of material must be measured with great accuracy[1,2]. However, such apparatus is quite unsuitable for normal laboratory-scale hydrogenations. The small number of hydrogenators intended for synthetic work vary from simple devices[3,4,5,6], to those which are exceedingly complex[7]. The simpler designs are divisible into two groups; one kind will handle large volumes of hydrogen with ease and fair accuracy of measurement, but is somewhat inaccurate for quantities of 1 litre or less[5,8]. The other type is capable of dealing with small quantities with good accuracy, but requires too much refilling when large volumes are required[3,4,6].

In the present design an attempt has been made to produce a robust apparatus having as many advantages as possible compatible with simplicity of construction and safe operation; its main features are shown in the theoretical diagram (Fig. 1). The apparatus is easily moved from bench to

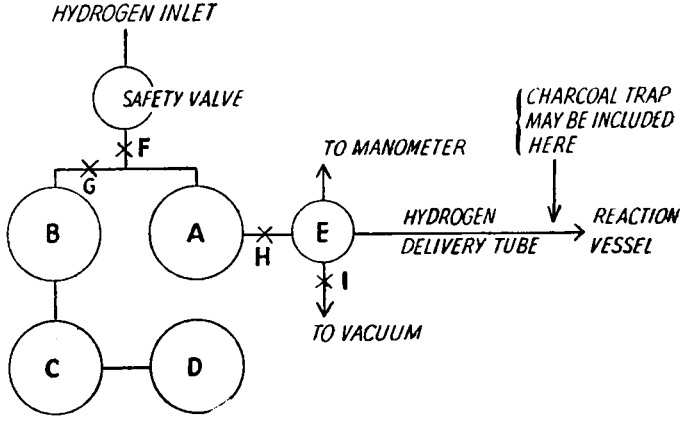

Fig. 1.—Theoretical diagram × = tap

bench, since it has been built up on a laboratory trolley. Filling is almost instantaneous, for there is no large volume of liquid to displace, a decided advantage during large-scale hydrogenations. The hydrogen uptake is measured by means of a manometer in conjunction with a reservoir of known volume; this reservoir may have a capacity of either 1 or 4 litres, according to the position of a tap at the back of the apparatus. When the reservoir capacity is 1 litre, the delivery of a few hundred ml. of hydrogen results in a considerable fall in the manometer reading, which makes accurate measurement an easy matter. The 4-litre capacity is more convenient for larger volumes. During a series of small-scale hydrogenations, using the

1-litre capacity, the rest of the reservoir may be used for hydrogen storage, thus making the apparatus fairly independent of a cylinder.

The manometer has been placed in circuit at such a point that on closing the reservoir outlet tap the absorption rate, as measured by the manometer, is magnified. This interferes in no way with the initial and final measurements of the reservoir pressure, and is most useful for observing the rate of hydrogen absorption. The maximum pressure obtainable is about 2 atmospheres, but the apparatus will also operate at pressures below 1 atmosphere, a fact which may prove useful in the controlled hydrogenation of substances which absorb hydrogen with great vigour. In order to safeguard the operator, a safety valve has been incorporated, which cannot fail to leak above a predetermined pressure. An efficient charcoal trap has been included for use on those occasions when it is thought that catalyst poisons are being introduced either from the hydrogen used or from the apparatus itself.

The Reservoir.—This comprises four 1-litre bolt-head flasks, A, B, C and D, each flask being closed by a well-fitting rubber bung, through which the necessary connecting tubes pass. After wiring in the bungs, each flask is wrapped in cotton material and secured to a cork ring by means of insulation tape, so that the flasks are protected during movement of the apparatus. The four flasks are mounted on the lower tier of the trolley and are kept in fairly rigid and symmetrical arrangement by means of a length of brass strip, which is looped around each flask neck, and serves to keep the flasks about three inches apart. The reservoir compartment is covered in with thick plywood in order to protect the operator, whilst tap G, which controls the reservoir capacity, is mounted so that it projects through a hole in the board at the back of the reservoir compartment. The reservoir inlet and outlet taps, F and H, are mounted onto a plywood frame, screwed to the back of the manometer upright (Fig. 2). This reservoir system may be replaced with steel flasks if required.

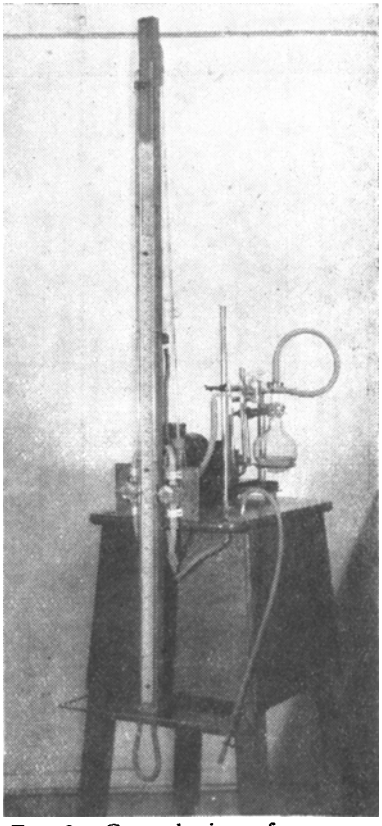

FIG. 2.—General view of apparatus

The Junction Tube.—The reservoir outlet tap, H, leads to a junction tube, E, in order to effect the connections referred to in the theoretical diagram. This consists of the open end of a thick-walled Pyrex boiling tube joined on to a length of 12 mm. tubing. Three side arms of the same tubing are then blown into the body of the boiling tube. The junction tube is situated in the reservoir

compartment, whilst the exhaust tap, I, is mounted in a rubber bung, which is fitted into a hole on the top of the trolley.

The Manometer.—An upright of oak ($\frac{7}{8}$" × 1$\frac{1}{2}$") screwed to the edges of the upper and lower tiers supports a metre scale, which slides up and down the upright between two accurately fitted wooden rails. The manometer itself consists of two lengths of thick-walled capillary tubing (internal diameter = 1·5 mm.; external diameter = 6·5 mm.) joined together at the bottom of the " U " by means of a short length of pressure tubing. The use of pressure tubing in this case not only simplifies construction of the manometer and renders it less fragile than an all-glass U-tube, but enables one to vibrate the mercury column before reading to ensure that tailing has not distorted the levels. The two limbs of the manometer are fixed to the rails on the upright by loops of copper wire at intervals; the wire passes around the back of the upright, but not across the metre scale. In filling the manometer air bubbles should be removed by forcing the mercury into the open limb and pushing a long length of copper wire down the tube.

The Safety Valve.—The principle of operation is as follows (see Fig. 3). As the pressure in the flask, L, increases, mercury is forced into the vertical capillary tube OM; the quantity of mercury initially in L is adjusted so that, when the pressure has risen to about 2 atmospheres, the whole of the mercury is in the vertical tube. A further small increase in pressure then forces the mercury into the baffle chamber, J. Hydrogen escapes through the outlet tube K, which contains a small quantity of mercury to act as a seal, during evacuation of the apparatus; the outlet of K is fitted with a miniature mercury baffle. During this process the pressure in the apparatus falls rapidly, and the hydrogen supply must be cut off completely before the mercury in J will again return to the flask, L. Both L and J are constructed from 50-ml. Pyrex flasks, J being the most simple and efficient mercury baffle of several types tried. The tube ON has the same dimensions as that used for the manometer and passes to the bottom of the vessel, L, which is mounted on the bottom of the reservoir compartment as near to the manometer upright as possible. Connection between ON and J is made with a length of capillary pressure tubing, MN; this should be kept reasonably straight. The use of narrow-bore tubing in this part of the valve reduces the volume of mercury required, and hence lessens the problem of baffling; the baffle, J, is mounted on a bracket, screwed to the back of the manometer upright. After J, ordinary pressure tubing is used in order to reduce the resistance to hydrogen

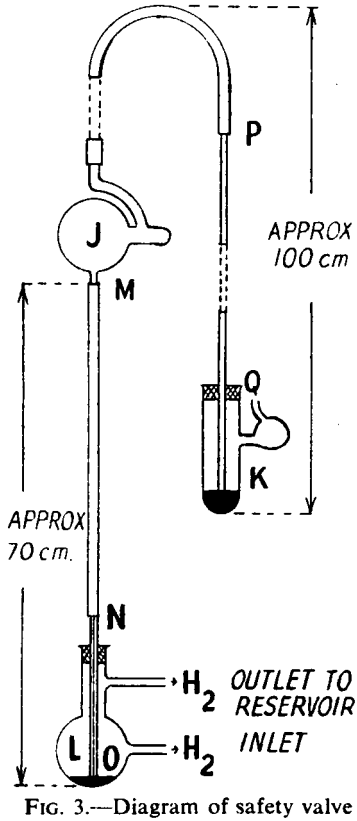

FIG. 3.—Diagram of safety valve

flow; PQ is a length of 6 mm. tube, which passes to the bottom of tube K; the latter is mounted on the top of the trolley immediately behind the manometer upright. The introduction of the correct volume of mercury is an

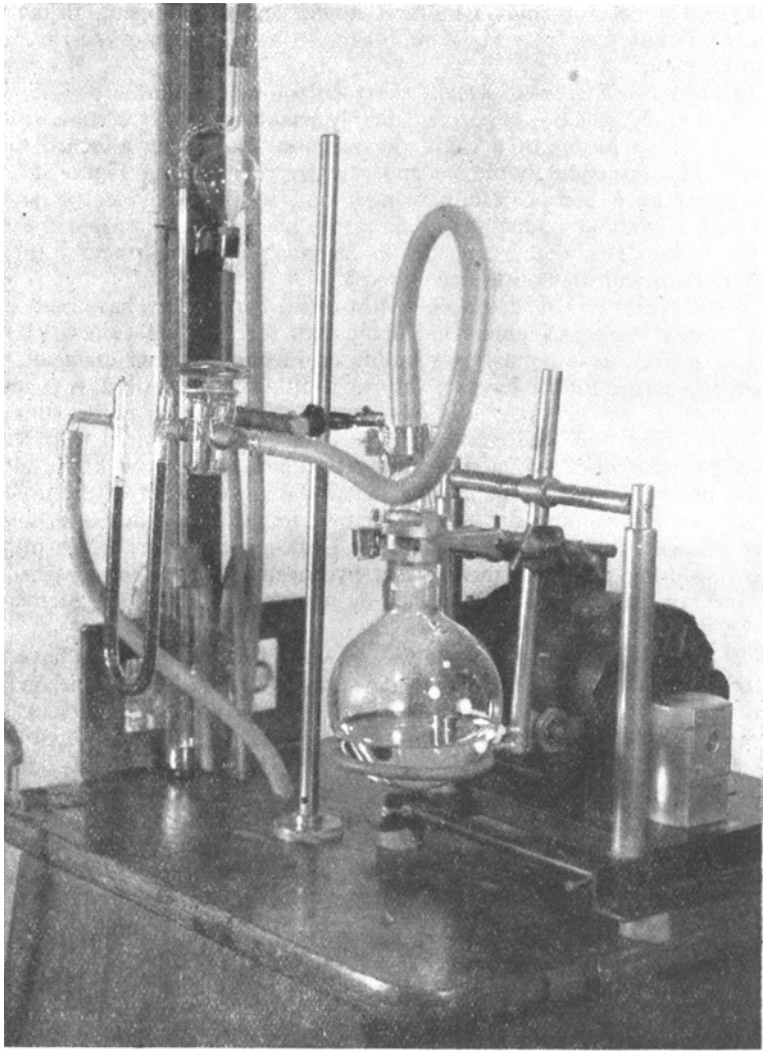

FIG. 4.—Close-up view of apparatus

easy matter; after removing the pressure tube from the top of J, small quantities of mercury are poured in until by trial and error the valve is found to operate at the desired pressure.

The Charcoal Trap.—When immersed in an acetone/solid carbon dioxide bath, this trap is capable of adsorbing 1 litre of hydrogen sulphide; it is therefore a useful adjunct where it is desired to rigidly exclude any catalyst poisons arising from the apparatus or the hydrogen supply. The construc-

tion should be apparent from Figure 4; the U-tube is filled with granular charcoal to give a total path of about 30 cm. length, and a glass wool plug is present at each end to prevent movement during the flow of gas. After use, immerse the trap in boiling water and pass a slow stream of hydrogen through for about an hour. At the end of this operation the trap should be quite free from moisture, otherwise it may block during the next hydrogenation.

The Shaker.—This was specially designed for the apparatus by Dr. W. J. Arrol. The 1/25th h.p. motor is suitably geared down to drive a rocking retort-stand by means of a shaft, the reaction flask being attached to the stand. The principle should be apparent by reference to Figure 4. The dimensions have been carefully worked out, so that the catalyst is very well shaken without undue splashing of the reaction mixture into the neck of the flask. This shaker appears to be much more satisfactory for this purpose than any previously encountered.

General Notes on Construction.—Most of the connections have been made with Portex Plastic Commercial Tubing No. 6c, and the associated glass work has been made from Pyrex tubing of 12 mm. external diameter, with which the plastic tubing forms a very tight-fitting joint. All glass junctions are narrowed at the tips and well-rounded off to facilitate the fitting of the plastic tube. In addition, each connection is doubly wired with No. 18 S.W.G. copper wire. When operating at 60 cm. of mercury above atmospheric pressure, the leakage rate of the whole apparatus is of the order of about 2 mm. an hour; for the 1 litre reservoir capacity this is equivalent to a leakage of approximately 3 ml. of hydrogen an hour, which may be ignored during any but the slowest hydrogenations. When desired, the leakage rate can be reduced further by working at a few cm. of mercury above atmospheric pressure.

The Taps.—Figure 5 shows the way in which high vacuum taps have been adapted to withstand pressure. The taps are well greased with Apiezon "L," and a slotted brass disc seated upon a rubber washer is wired into place, so that the tap is held firmly into its socket. This method has given very little trouble.

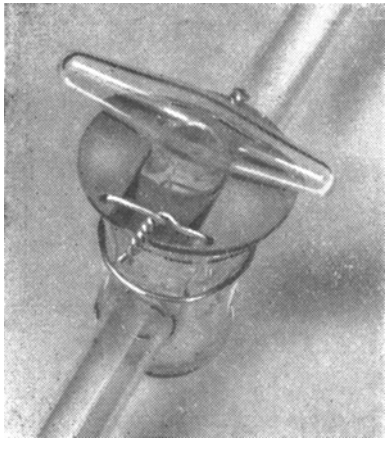

FIG. 5.—Close-up view of a tap

Calibration.—It is necessary to know the precise volumes of the reservoir when set at nominal capacities of 1 and 4 litres respectively. The apparatus should be filled with hydrogen and the drop in manometer pressure noted during the delivery of 500 ml.; a volumetric flask and a trough of water at room temperature is useful here. The volumes are then readily obtainable after correcting for aqueous vapour pressure. It is useful for practical purposes to calculate approximately the fall in manometer pressure corresponding with the delivery of 100 ml. of hydrogen in the case of both reservoir capacities. As will be seen below, in calculating the manometer drop for a given hydrogenation it is necessary to add the volume of

the dead space in the reaction vessel to the reservoir volume before arriving at the final volume for calculation purposes.

Calculation of Reservoir Volume.—Suppose 500 ml. has been collected over water at room temperature.

Let v = volume of reservoir in ml.

m_1 = initial manometer reading in mm.

m_2 = final manometer reading in mm.

a = atmospheric pressure in mm. of mercury

w = aqueous vapour pressure of water at room temperature in mm. Hg

$$\text{Then } v = \frac{760 \times 500}{(m_1 - m_2)} \left(1 - \frac{w}{a} \right)$$

Mode of Operation

(a) *Filling With Hydrogen.*—Close the hydrogen delivery tube by means of a pinch clip or, if the charcoal trap is being used, close the tap thereof. Connect the exhaust outlet to vacuum and close tap F; open taps G, H and I, and evacuate the apparatus. Then attach the hydrogen inlet tube to a cylinder and sweep out the air in the safety valve and associated tubing by applying just enough pressure to blow the valve, and then allowing hydrogen to bubble through for a few seconds. If the inlet tube is detached from the cylinder without previously closing by means of a pinch clip, air will diffuse into the valve, and must be swept out again before refilling. The apparatus is then filled by opening tap F and allowing hydrogen to flow in from the cylinder until the manometer registers about 60 cm., when tap F is closed. Tap H must be open during this operation. This sequence of operations is sufficient when the apparatus is in regular use, but when first used or after being unused for some time it is advisable to sweep out the apparatus thoroughly by repeating the above sequence two or three times, depending on the vacuum available.

(b) *Hydrogenation.*—A standard joint round-bottomed flask of suitable capacity is used as reaction vessel, and an adapter is needed to connect to the hydrogen delivery tube. The adapter is made by pulling out a standard cone and joining on to a short length of 12 mm. Pyrex tubing. The joint is greased with Apiezon "L" and held together by copper wire in conjunction with two bands of brass strip, as shown in Figure 4. Estimate, or measure when maximum accuracy is required, the dead space which will exist in the flask and adapter after adding the solution to be hydrogenated. This volume is added to the appropriate reservoir volume before calculating the manometer fall, which corresponds with the theoretical volume of hydrogen to be absorbed (see below). Then check that tap G is set to the desired reservoir capacity and close tap H. Mount the reaction vessel on the shaker and connect the adapter to the hydrogen delivery tube, open the tap on the charcoal trap, if this is in circuit.

Evacuate the reaction vessel by opening tap I, and after closing it admit hydrogen from the reservoir. Whether or not this operation is repeated depends upon the vacuum available and the volatility of the solvent, although where possible it should be repeated. At this point tap H should be open; if the manometer reading is too low, let in more hydrogen from the cylinder or, when the 1 litre capacity is being used, it is only necessary to open and close tap G. Note the manometer reading, making sure that tap F is closed and tap H open; start the shaker. In order to check that hydrogen is being absorbed, it is useful to close tap H at this point in

order to obtain the magnified pressure fall referred to above. During very slow hydrogenations it is advisable to correct for any change in atmospheric pressure and room temperature that has occurred during the process and to adjust the final manometer reading accordingly.

Calculation of the Required Manometer Drop

Let t_1 = temperature (in °C.)
s = volume of the dead space (in ml.)
h = volume of hydrogen in ml. theoretically required at N.T.P.
(The other symbols are as above)

$$\text{Then } m_1 - m_2 = 760 \times \left(\frac{h\,(273 + t_1)}{273\,(v + s)} \right)$$

Correction for Temperature and Pressure Variations During Hydrogenation

Let m_2 = the originally calculated final manometer reading (in mm.)
m_3 = the corrected final manometer reading (in mm.)
t_1 = initial temperature (°C.)
t_2 = final temperature (°C.)
a_1 = initial atmospheric pressure (in mm. mercury)
a_2 = final atmospheric pressure (in mm. mercury)

$$\text{Then } m_3 = \left(\frac{(273 + t_2)\,(m_2 + a_1)}{(273 + t_1)} \right) - a_2$$

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