[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

A STOPCOCK IN WHICH CONTAMINATION BY GREASE IS PREVENTED AND ITS APPLICATION TO A PROBLEM IN GAS TECHNIQUE

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Vapors from stopcock grease are always more or less objectionable in high vacuum work, but greased stopcocks have frequently been tolerated when gases under moderate pressure were to be transferred through such a system in roughly controlled amounts. The objection to stopcock grease is more serious when organic vapors are to be handled, for in many cases these vapors are taken up in appreciable amounts by the stopcock grease. This is the case in a problem in reaction velocity which the author wished to undertake, and the apparatus here described was successfully used in that work.

The principle is illustrated by Fig. 1A.

This stopcock is of the hollow plug type. The ground portion is about 4-cm. long. A small groove is ground on the outside of the plug, completely encircling it at about two-thirds of the way down the ground portion as shown at a. Two vertical grooves are etched on the inside of the bore of the stopcock from the top of the ground portion down sufficiently far to reach the circular groove when the plug is in place. They are shown in the cross-sectional diagram, Fig. 1B, at b. They are about 1 mm. wide and probably about 0.1-mm. deep. They are produced by etching with concentrated hydrofluoric acid for about twenty minutes.

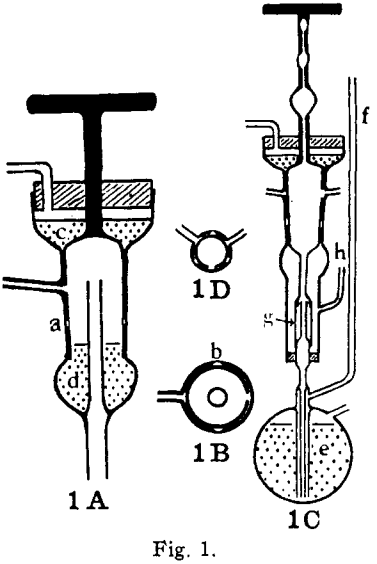

Fig. 1.

The stopcock is assembled as follows. A very small amount of stopcock grease is applied to the lowest edge of the ground portion of the bore and the plug inserted with the hole of the plug in line with the side opening on the bore. If now the system is evacuated, mercury from above the plug at c will flow down the two vertical grooves and into the circular groove. Gas flowing through the stopcock cannot come in contact with the stopcock grease on the lower ground portion, for it is protected between the ground surfaces by the ring of mercury, and from the inside by the mercury at d. To close the stopcock the plug is turned through 180° as shown in Figure 1B. In this process a very small droplet of mercury falls through the hole as the hole passes one of the grooves. It is apparent that the stopcock will not allow gas to pass if the pressure on either side of the stopcock is a few cm. less than the external pressure forcing the mercury into the grooves.

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The success of such a stopcock depends on the fact that surface tension prevents the mercury from going beyond the edges of the grooves, which it will not do if the surfaces are sufficiently close fitting. If, however, they fit very tightly, the stopcock cannot be turned. The purpose of the grease in the lower portion is to give a slight separation so that the stopcock may be turned easily. It was found that from 40 to 50 cm. difference in pressure was the upper limit for which the mercury would not leak through and the stopcock could yet be turned. It was, therefore, necessary to control the external pressure by placing a rubber stopper over the top of the stopcock, thereby making it possible to control the pressure on the mercury at c. The hole in the stopper through which the handle of the plug passes is greased and remains airtight.

It was convenient in the study of the thermal decomposition of the gas methyl *iso*propyl di-imide to be able to introduce a measured amount of gas from a supply bulb into the reaction cell, and to measure the pressure in the cell immediately and at intervals during the reaction. In another research it was necessary to introduce into the reaction cell a definite pressure of azomethane gas mixed with varying amounts of some inert gas, and then to follow the decomposition of the azomethane by pressure measurements. If this were attempted using ordinary greased stopcocks the partial pressure of azomethane would change during handling of the gases, due to absorption by the grease.

An application of the above described stopcock was devised for these experiments. It is illustrated in Figs. 1C and 1D.

The body of the stopcock is made as in Fig. 1A except that there are two side tubes and three vertical grooves as indicated in Fig. 1D. When this stopcock is in the closed position (Fig. 1D) it may be used as a McLeod gage, mercury being forced up from the bulb, e. Accuracy over a wide range of pressures is secured by placing bulbs of varying size in the handle of the stopcock. The gage is calibrated by determining the volumes to fixed points on the capillaries between the bulbs, and to a fixed point in the tube below the hollow plug. The one used in the experiments referred to has a total volume of 15.2 cc. and can measure pressures from 0.06 to 30 mm. with an accuracy varying between 0.2 and 2%. The tube, f, leads to a high vacuum. This tube is larger than the capillaries in the handle, so that with the gage evacuated the mercury in the tube, f, rises to a higher level than in the capillary. When the mercury is at one of the fixed points on the capillaries the mercury levels on the tube, f, are taken as the positions of zero pressure.

To allow the stopcock to turn and yet keep the mercury bulb, e, stationary, a rubber tubing connection is made at g. The space surrounding it is evacuated through the tube, h. When the mercury has once been run up through this rubber connection and has filled the rubber tube and the inner glass tube, no gas in the gage comes in contact with rubber tubing.

In using the device for the azomethane research, azomethane was introduced through the left tube. The flow could be controlled readily, since the gas could be made to pass between the ground surfaces to reach the hole. The stopcock was closed and the pressure measured. Azomethane was pumped out of the left tube and an inert gas under pressure was then similarly admitted. The total pressure was then determined. The gases were thoroughly mixed by the compression and expansion during the

pressure measurement. The mixed gases were admitted to the reaction cell, which was attached close to the right-side tube. The stopcock was then closed and the pressure read at liberty. At any predetermined time the stopcock was opened for a few seconds and another pressure measurement made. The rate of this reaction could thus be followed, since an increase in pressure at constant volume occurs in the reaction.

It is evident that at no time after the gases were once admitted to the gage did they come in contact with grease. The device is very compact when one considers the number of operations to be performed.

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THE THERMAL DECOMPOSITION OF METHYL ISOPROPYL DI-IMIDE: A HOMOGENEOUS UNIMOLECULAR REACTION. THE THERMAL DECOMPOSITION OF HYDRAZOIC ACID AND METHYL AZIDE

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It is important that present theories of unimolecular reaction velocity should be thoroughly tested with a wide variety of reactions. All homogeneous unimolecular gas reactions so far discovered involve rather large molecules. Their reaction rate is too fast to be accounted for without ascribing to some of them as large a number of internal degrees of freedom as can be justified, while others require but few degrees of freedom. The decomposition of nitrogen pentoxide cannot at present be accounted for in this way, but the low-pressure data may still be questionable.

The author had previously found that the two azo compounds, azomethane[2] and azo-*iso*propane[3] decompose in a homogeneous unimolecular manner. A new azo compound, methyl *iso*propyl di-imide was recently prepared[4] by the author to provide an additional test of unimolecular reaction rate theories. Its decomposition will be shown to be first order at high pressures. However, the rate constant becomes lower at low pressures, as was also the case with azomethane.[5]

A unimolecular reaction involving a smaller molecule with a more limited number of degrees of freedom would provide another valuable test of reaction rate theories. For this reason the decomposition of hydrazoic acid and methyl azide was studied.

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[2] Ramsperger, THIS JOURNAL, **49**, 912 (1927).
[3] Ramsperger, *ibid.*, **50**, 714 (1928).
[4] Ramsperger, *ibid.*, **51**, 918 (1929).
[5] Ramsperger, *ibid.*, **49**, 1495 (1927).