[CONTRIBUTION FROM THE CHEMICAL SCHOOL OF THE UNIVERSITY OF MELBOURNE]

A NEW FORM OF BUBBLE COUNTER FOR MEASUREMENT OF GAS EVOLUTION

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RECEIVED MAY 15, 1930 PUBLISHED JULY 8, 1931

The measurement of the volume of gas evolved during the progress of a reaction in which a gas is one of the products is a well-known method of measuring reaction velocity coefficients. The estimation of the rate of evolution of the gas by timing evolution of gas bubbles of uniform volume is a very attractive experimental method, and if the counting can be performed automatically the method becomes almost ideal. Various appliances to carry out bubble-counting of this kind have been described in the literature at various times. For instance, Bose[1] has used such a method in his studies of photosynthesis.

During an investigation on the rate of decomposition of hydrogen peroxide in the presence of hydrochloric acid, the author was led to devise an apparatus which proved quite useful for the purpose. The starting point was a simple apparatus which was in use in England.[2] In this apparatus, however, the bubbles were formed at the mouth of a bell-shaped tube immersed mouth-downward in a vessel of water. It was found that this form of bubbler was unsatisfactory, as the volume of the bubbles was not constant under varying rates of bubbling and over long periods. Finally the author devised the form of apparatus shown in Fig. 1.

In this figure, A shows the top of the reaction flask, from which the gas to be measured (in this case oxygen) is being evolved. The gas passes by way of the rubber connection B and the tube C to the bubbler D, which is immersed in the water of the thermostat. The gas issues from D in distinct bubbles of constant size. This constancy of size is ensured by the U-shaped bend of capillary tubing which is so fused on that the change of internal diameter shall be as sudden as possible. On account of the surface tension of the water in the capillary tube, the meniscus does not leave it; the bubble breaks off when the gas–water interface has reached F and the interface immediately retreats to E. The volume of the bubble is therefore rigidly defined by the dimensions of this capillary in comparison with the total volume of gas space in the apparatus. Each time a bubble breaks away there is a diminution in the pressure of the gas enclosed in the apparatus. This variation of pressure causes an oscillation in the level of the mercury in the U-shaped tube G, and this oscillation is made to operate an electrical make-and-break by means of a platinum wire H sealed through the lowest part of the U and another platinum wire J so arranged that the mercury in rising will make contact with it. When a bubble breaks away from D and the gas–water interface moves smartly from F to E, the sudden fall of pressure causes the mercury in G to fall rapidly away from the platinum wire J and thus break the circuit. In this circuit is a 2-volt battery, a regulating resistance and a relay. This relay switches on and off a stronger current fur-

[1] Bose, "The Physiology of Photo-synthesis," Longmans, **1924**, p. 21.

[2] *School Science Review*, **4**, 139 (1923). (A more detailed description which was referred to in this review could not be traced.)

nished by a 60-volt battery which operates a counter such as is used for counting telephone calls. The make and break of this higher-voltage circuit is through a pair of arc light carbons, one of which is furnished with a screw adjustment. By this means fouling of the contacts owing to sparking is rendered innocuous. There are a few further points worth mentioning with regard to the low-voltage contact G. A large part of the U-tube of G is made of capillary tubing in order to render the contact "dead beat" in its action by damping out oscillations of the mercury column which might lead to false contacts. A few drops of distilled water are placed above each mercury surface in G to act as a lubricant and prevent sticking of the mercury. To minimize sparking when contact with the wire J is broken, a condenser is placed in parallel with this gap. The absolute elimination of sparking at this contact is desirable, as it results in fouling of the contact and uncertain counting during the course of a long run. This sparking causes a brownish cloud, presumably finely divided mercury, to form in the water. This can be removed by flushing out the widened portion of the tube with distilled water from a wash bottle with a fine jet. If the surface of the mercury becomes covered with a scum, this is removed by adding a trace of nitric acid to the water by touching it with a platinum wire that has been dipped in dilute nitric acid. If this is done, the wide tube must soon afterward be well flushed out with water, as otherwise a deposit of mercurous nitrate will soon put the contact out of action. Contact was found to be more certain when the platinum wire J was connected to the positive pole of the cell, owing to the well-known effect of the nature of the charge of a mercury surface on its surface tension. As the mercury rises toward J its potential is negative toward the water and in consequence the increase of surface tension tends to depress the meniscus; but as soon as the mercury touches the wire J, this negative potential becomes zero. In consequence the surface tension decreases and the resulting small rise of the mercury meniscus renders contact certain and the mercury appears to adhere to the wire. When the mercury meniscus is jerked away from the wire as a bubble breaks away at D, the depression of the meniscus, due to the increased surface tension, effectively prevents any second contact. This phenomenon was found to be a very important protection against the effects of chance vibration. The point needing most attention, however, is the preservation of a bright clean surface at the mercury meniscus by the prevention of sparking. This calls for a small current at the contact J and a sensitive relay. The clicking of the counter could be heard even in an adjacent room and, although this is rather trying to the nerves over a long period, one subconsciously listens to the clicks and soon learns to appreciate the slightest variation from regular working, which gives timely warning of any incipient trouble at the contact.

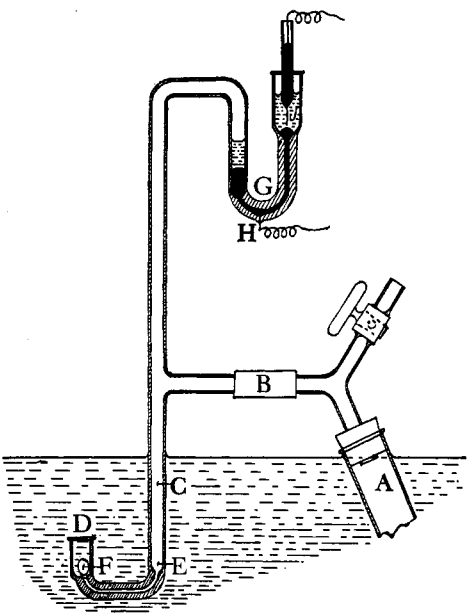

Fig. 1.—Diagrammatic view of the bubble counter.

For testing the equality of the volume of the bubbles a useful accessory is a piece of capillary tube of suitable internal diameter, which is placed horizontally against a scale and calibrated by a mercury thread in the usual manner. One end of this capillary is bent vertically downward and expanded into a bell-shaped mouth. This dips below the water in the bath and enables a single bubble to be caught. The other end of the capillary is also bent downward and carries a stopcock. When the tube is filled with water, it acts as a siphon and by opening the stopcock the bubble caught in the bell may be brought to a convenient place in the tube for measurement of its volume.

A serious limitation on the usefulness of the apparatus lies in the necessity for the constancy of the total volume of gas in the tubes of the counter and any apparatus to which it is connected. Also this gas volume must not be too large or a series of bubbles is formed at each emission instead of a single one. A gradual change in this gas volume can be allowed for by measuring the volume of the bubbles at various times by means of the accessory capillary tube; but, where this gas volume is not subject to change, the apparatus is very convenient for such purposes as the measurement of reaction velocity by gas evolution, since both the total volume of gas evolved and also the rate of evolution of the gas are easily obtained by readings of the dial.

The author desires to express his sincere thanks to Professor E. J. Hartung for the generous manner in which he has made available facilities for carrying out this work and for his very helpful criticism and advice.

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INACCURACY IN THE DETERMINATION OF MERCURY BY DIRECT PRECIPITATION AS MERCURIC SULFIDE FROM ACID SOLUTION[1]

BY E. P. FENIMORE AND E. C. WAGNER

RECEIVED NOVEMBER 18, 1930 PUBLISHED JULY 8, 1931

The direct precipitation of mercury as sulfide from acid solution is a procedure whose accuracy has for many years remained apparently unquestioned.[2]

[1] This paper is constructed from a portion of the doctorate thesis of Edward P. Fenimore, University of Pennsylvania, 1929.

[2] Fresenius–Cohn, "Quantitative Chemical Analysis," John Wiley and Sons, Inc., New York, **1903**, Vol. I, p. 366; Rüdisüle, "Nachweis, Bestimmung und Trennung der chemischen Elemente," Drechsel, Bern, **1913**, Vol. II, p. 412; Treadwell–Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, **1924**, Vol. II, 6th ed., p. 172.