generator, hence there can be no leakage of acid or gas as a result of deteriorated fittings.

4. The apparatus is controlled by causing the gas to pass through a small opening. As there are no small tubes through which the acid must pass, commercial acids containing solid impurities may be used, if desired.

5. The apparatus is more easily accessible than any other, hence is more easily cleaned, and may be charged with larger lumps of iron sulfide than is possible where access to the interior is through a small opening only.

6. The generator has a larger storage capacity for gas than any other self-contained apparatus, hence is less likely to overflow, owing to a lack of storage capacity, when the gas is shut off.

7. The generator operates on the principle of delivering small quantities of acid into the iron sulfide chamber, which is generally admitted to be the best.

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A NEW FORM OF ULTRA-FILTER: SOME OF ITS USES IN BIOLOGICAL AND SYNTHETIC ORGANIC CHEMISTRY.[1]

By Philip Adolph Kober.

Received February 27, 1918.

I. Introduction.

Ultra-filtration has hitherto meant filtering through semi-permeable membranes, which were used, until recently, for the separation of "crystalloids" from "colloids." To-day it has a broader meaning; signifying the separation, by filtration, of the relatively small molecules from those relatively large.

Through the work of Bechhold,[2] Walpole,[3] Brown[4] and others, a substantial start has been made in the development of selective filtration. These investigators describe membranes of almost any degree of permeability which were made by them. Bechhold and Walpole showed that dialysis could be used for ultra-filtration purposes, if it were not for the enormous dilution of both filtrate and residue caused by the dialyzing water. As some of the dialyzable constituents diffuse out of the membrane, the remainder becomes dilute, due to endosmosis, and the speed

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[1] Read before the Biological Section, American Chemical Society, Boston, Mass., Sept. 11–13, 1917.

[2] *Z. physik. Chem.*, **60**, 259 1907).

[3] *Biochem. J.*, **9**, 285 (1915).

[4] *Ibid.*, **9**, 591 (1915); **11**, 40 (1917).

and efficiency of dialysis is, in consequence, reduced in proportion. The more one attempts to dialyze quantitatively, the more dilute will the respective residue and filtrate become, and thus it is difficult, if not impossible, to have quantitative dialysis. For the above reason, therefore, practically all ultra-filtration work has been done with high pressures and special apparatus.

Through the discovery that all these membranes pervaporate,[1] the difficulties of ultra-filtration by dialysis have been completely overcome. The advantages of filtration by dialysis are: (1) no pressure apparatus is necessary; (2) since textile strength need not be considered, a greater latitude is given to the texture or composition of the membranes; (3) the stretching of the membrane caused by pressure is eliminated, thus allowing a finer and a more accurate graduation of permeability, and (4) no attention is necessary once the process in started.

The Apparatus.

Fig. 1 shows a simple laboratory arrangement for ultra-filtration. It consists essentially of a dialyzer, A; and a pervaporator, B; connected by a syphon. The dialyzer has an automatic water supply, D. The pervaporator concentrates the diffusate, obtained from the dialyzer. The water of the dialysate is pervaporated from the upper part of the dialyzer with the aid of fanning. As the contents of the dialyzer decreases the counter weight raises it partly out of the dialyzing bath, so that the residue at the end is practically pervaporated to dryness. This, however, cannot take place while there is endosmosis (due to any dialyzable constituent within the container); therefore the dialysis must be quantitative. By regulating the amount of water supply, so that it can either be

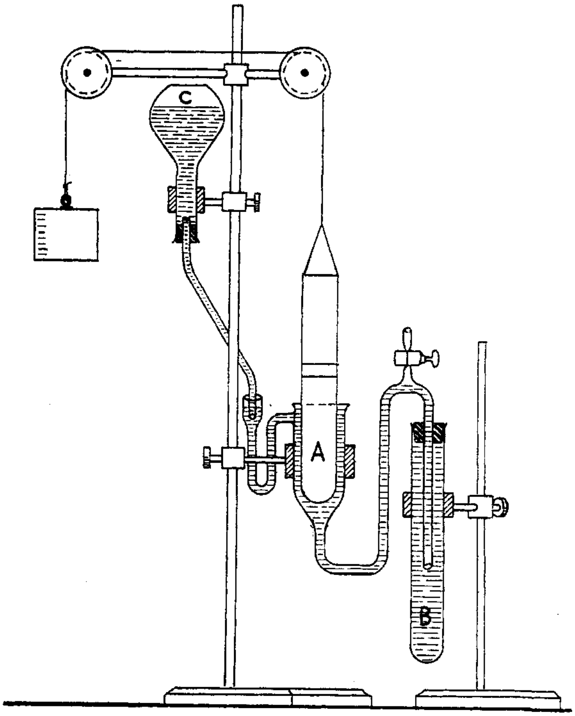

Fig. 1.

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[1] Kober, This Journal, 39, 941 (1917).

stopped or made to cease, when dialyzation is finished, the diffusate, or filtrate, can be obtained in any volume or form desired, by continuing the pervaporation. For these dialyzers ordinary collodion has two disadvantages, *viz.*, (1) when pervaporated from one side, the great shrinkage that accompanies the drying, after the liquid is no longer in contact with it, causes the container to become distorted so badly that it is difficult to use it for this purpose; (2) when dry, these collodion containers, as is well known, become impermeable. Both of these obstacles can be circumvented by using the container anaerobically as follows: the container with its contents is evacuated until the collapsing walls force the liquid to the top, when the container is closed off or stoppered. It is more simple to compress the container by hand until the liquid rises to the top, when an air-tight stopper is inserted. If the container is large enough when full to take care of considerable endosmotic water which otherwise would burst the container, it will always have liquid in contact with its walls; and therefore there can be no appreciable shrinkage.

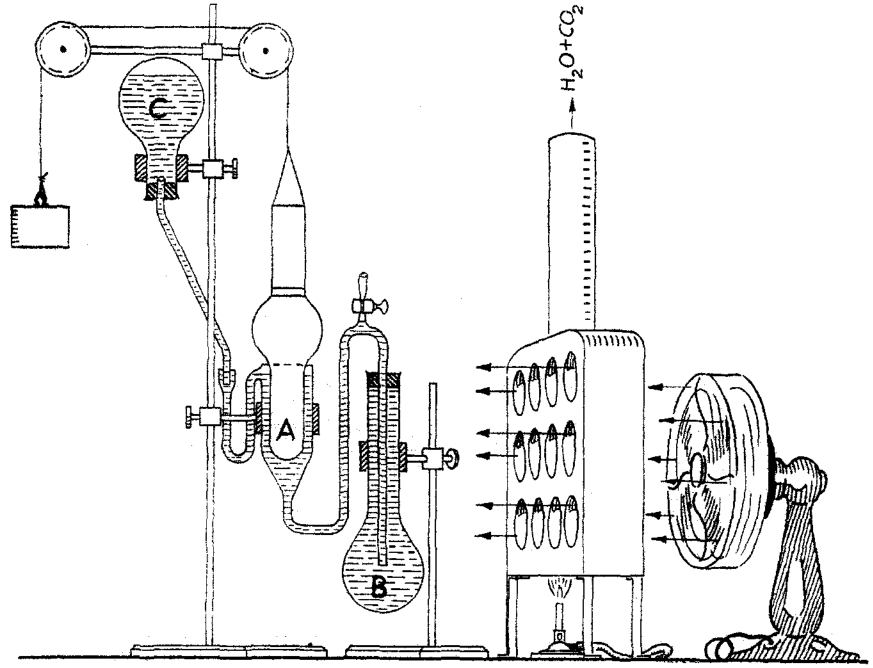

Fig. 2.

This method of using pervaporating containers is advantageous for ordinary pervaporation work, since it allows the pervaporation to proceed at almost an undiminished speed, because it keeps the amount of the pervaporating surface practically constant.

For some of the experiments referred to in this paper "Percollodion" containers[1] were used. Although they are not yet obtainable in graded permeabilities, they have none of the disadvantages of ordinary collodion just pointed out, *i. e.*, they do not shrink appreciably when dried and are permeable at once when used anew.

Another form of ultra-filter, shown in Fig. 2, permits the filtration of larger amounts of substance. On the right side of the figure is shown a hot-air radiator for use with an electric fan.

II. The Uses of Ultra-Filtration in Biological and Synthetic Organic Chemistry.

The idea of using dialysis for removing coloring matter is not new. Dubrunfaut,[2] in 1872, suggested it for removing the coloring matter from molasses. Presumably the dilution, resulting from dialysis, was too great an obstacle, however.

In biological chemical work, particularly in experiments upon hydrolysis and digestion, large amounts of black, carbonaceous and humus substances, as well as other coloring matters of unknown and high molecular weight, are obtained in side reactions. By ultra-filtration through membranes all of those non-dialyzable impurities can be removed quantitatively. Thus, for example, in the isolation of histidine from the hydrolysis of some blood-clots, after repeated use of various charcoals, the histidine solutions and crystals were highly colored with dark brown humus material. By one filtration through the ultra-filter, a solution was obtained with only a slight straw color. Besides, the apparatus should prove useful even for analytical work in removing proteins and other non-dialyzable substances from solution, and in general for quantitative dialysis.

In organic synthesis highly colored complexes are often found which are a great hindrance to rapid and accurate work. As an example, recently in some synthetic work a fusion product was so highly colored that it was opaque even in thin layers. Charcoal and other methods of treatment effected no decided improvement, but with ultra-filtration a practically colorless solution was obtained.

The advantages of this method of removing coloring matter are: (1) it is quantitative; (2) it requires no attention, once the process is started; (3) it concentrates both residue and filtrate; (4) it can be conducted at a low temperature, so that even very sensitive substances can be safely treated.

To obtain its maximum usefulness, much work yet remains to be done

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[1] Made by Klett Manufacturing Co., Inc., 202 East 46th St., N. Y. They are prepared to furnish the whole outfit, including glass and metal parts.

[2] "L'Osmose et ses Applications Industrielles," by Dubrunfaut, Paris (1873).

on various kinds of membranes, their permeabilities and properties. Brown[1] has shown that membranes allowing dialysis in almost any sort of solvent, even such as alcohol, acetone, glacial acetic acid, toluene, benzene, etc., can be made. This indicates that pervaporation and ultrafiltration are by no means limited to aqueous solutions.

Summary.

A new form of ultra-filter has been described which depends on pervaporating both the dialysate and the diffusate solutions during dialysis.

Its usefulness in biological and synthetic organic chemistry for the removal of humus, coloring matter and colloids in general, has been pointed out and illustrated.

The apparatus makes it possible now, for the first time, to dialyze quantitatively.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

GLACIAL ACETIC ACID AS A SOLVENT FOR PRUSSIC ACID. BENZALHYDRAZINOPHENYLACETONITRILE AND SOME DERIVATIVES.

BY J. R. BAILEY AND R. H. PRITCHETT.

Received May 17, 1918.

Introduction.

Bailey and co-workers have recently reported investigations[2] of the use of cyanic acid in glacial acetic acid, and this work very naturally suggested the use of prussic acid in the same solvent. Work in this direction had been under way for some time, when in *Chemical Abstracts* there appeared a reference to an article by R. von Walther and R. Hübner entitled "Conversion of Aldehydes and Ketones into α-Amino Nitriles and Derivatives of the Latter." The very efficient method of preparation used here is to dissolve an aldehyde or ketone together with a suitable amine in glacial acetic acid and add potassium cyanide, *e. g.*, phenylaminophenylacetonitrile, $C_6H_5NHCH(CN)C_6H_5$, is conveniently made by allowing benzaldehyde, aniline, and potassium cyanide to react in glacial acetic acid "to which a little water is added." As Walther and Hübner have undoubted priority in this work, and it is their announced intention to continue the investigation on the use of prussic acid in glacial acetic acid, we have no desire to interfere with their problem, and will simply announce the results obtained by us in this direction. The article of Walther and Hübner referred to above appeared[3] in 1916, but,

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[1] *Loc. cit.*

[2] THIS JOURNAL, **37**, 940, 1884 (1915); **39**, 279 (1917).

[3] *J. prakt. Chem.*, **93**, 119 (1916).