[CONTRIBUTION FROM THE DIVISION OF LABORATORIES AND RESEARCH, N. Y. STATE DEPARTMENT OF HEALTH.]

PERVAPORATION, PERSTILLATION AND PERCRYSTALLIZATION.[1]

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I. Introduction.

In the course of some experiments on dialyzation, my assistant, Mr. C. W. Eberlein, called my attention to the fact that a liquid in a collodion bag,[2] which was suspended in the air, evaporated, although the bag was tightly closed. At first we were inclined to ascribe it to evaporation through a small aperture at the top of the bag, but further experiments and especially the speed of evaporation soon forced us to the conclusion that the aqueous vapor is given off through the membrane, as though the water were suspended as a solid without any membrane present. This phenomenon we have named pervaporation. The speed of this pervaporation is so great that with ordinary heating facilities such as a Bunsen flame and electric heaters, it has been impossible to heat water to a boil.

Distillation by means of pervaporation, we have called perstillation. When a dialyzable solute within the membrane container reaches saturation, it crystallizes out on the outside of the membrane. This phenomenon we have named percrystallization. In order to show some of the possible uses of these phenomena, the following experiments are described:

II. Experiments.

1. Pervaporation. (*a*) *Spontaneous.*—Two collodion containers were made in the shape of a "300 cc." Kjeldahl flask. Into each collodion container were placed about 325 cc. of a solution containing serum albumin and about 25 cc. toluene. The top of the containers were tied as tightly as possible and suspended in a warm room at about 37°. After fanning these containers with an ordinary office fan for 24 hours the aqueous layer had pervaporated to dryness, while considerable toluene remained.[3] Two similar containers, but having a glass top and closed with cotton and tin-foil, to prevent contamination as shown in Fig. 1, were sterilized and filled with 300 cc. sterile meat infusion broth media. After pervaporation in a large incubator, which was by no means dry, and without fanning,

[1] Read at the meeting of the Soc. Expt. Biol. Med., Feb. 21, 1917.

[2] I am indebted to Dr. A. B. Wadsworth, director of these laboratories for calling my attention to and for arousing my interest in collodion bags for dialysis, the use of which led to the observations described in this paper.

[3] Toluene seems to coagulate and render insoluble dry proteins-like albumin.

the contents were like Liebig's beef extract in color, taste and consistency. This is sufficient to show the possible usefulness of pervaporation in concentrating sterile preparations such as foodstuffs, toxins and anti-toxins, not only under sterile conditions[1] but also, it seems, anaerobically.

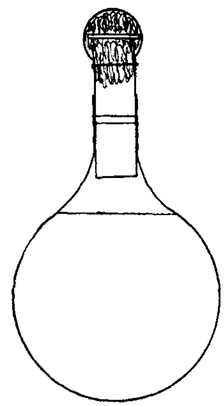


Fig. 1.
Sterilized Pervaporator

(*b*) *Pervaporation with Heat.*—A number of collodion containers were made, in the shape of test tubes, Erlenmeyer and round-bottom flask.[2] After shrinking the containers by placing them in boiling water for a few minutes, the following experiments were made:

A test tube container, closed at the top, with a thermometer attached, and filled with water, was heated with the bare Bunsen flame.[3] Although pervaporation proceeded so rapidly that the level of water sank like a slowly emptying buret, yet the water rose only to 70° at the start and as the pervaporating surface decreased with the sinking of the water level, the temperature only slowly rose to 75° when the experiment was discontinued owing to the danger of overheating the upper part of the tube. Other collodion test tube containers were placed on an asbestos gauze, with a strong flame underneath, but the temperature never rose above 60°.

To demonstrate further the absence of boiling with ordinary heating elements, an Erlenmeyer glass flask was filled with 500 cc. of tap water, slightly below room temperature. After introducing a "Hot-point" immersion heater of about 300 watts the contents were heated and stirred[4] for 13 minutes, when the water was in a vigorous boil, overflowing the flask. The boiling water was then put into a collodion container of the same shape, but which, owing to shrinkage, only held 400 cc. After stirring and heating with same immersion heater for 13 minutes, the water, owing to rapid pervaporation, did not come to a boil. During these last 13 minutes 130 cc. of water had pervaporated away.

The same collodion container with 340 cc. of water was placed on an

[1] Other experiments bearing on and proving sterile pervaporation will be described in a separate communication.

[2] Pervaporating, perstillating and percrystallizing vessels, containers and apparatus may be obtained from Klett Manufacturing Co., Inc., 202 East 46th St., N. Y. City.

[3] Collodion, when dry, will, as is known, burn somewhat like paper, when ignited. In two experiments the flame accidently ignited the upper part of the container. In both cases the flame was blown out and the contents saved.

[4] Owing to the short stem on the heater the water did not circulate without stirring.

asbestos gauze with a strong Bunsen flame underneath, the upper part of the container being tightly stoppered. A control experiment with the same flame and the same amount of water, showed that in a glass vessel it required but 8.5 minutes for the water to boil. At the end of 30 minutes' heating, the water in the membranes showed a temperature of 92° and had pervaporated to the extent of 150 cc.

2. Perstillation. (*a*) *At Ordinary Pressure.*—In using collodion containers where the distillate is also desired two methods of heating, electrical or steam may be used. In Fig. 2 is shown an electrical perstillator which is sufficiently clear without further comment. In Fig. 3 a steam perstillator is shown which may be connected to steam connections of a building or to separate steam boiler as also shown in Fig. 3. As will be

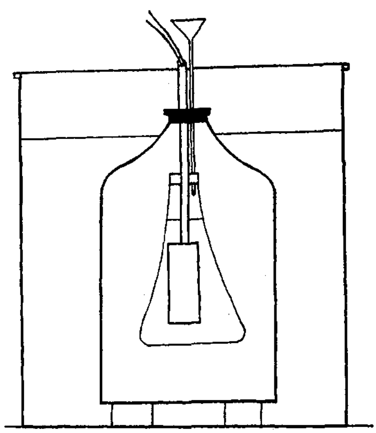


Fig. 2.
Electric Perstillator

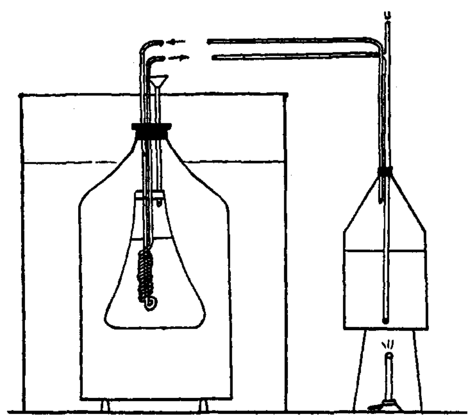


Fig. 3.
Steam Perstillator.

observed, owing to the low temperature of perstillation, ordinary bottles and glassware can be used as condensers to an advantage. The steam perstillator has the advantage of being free from overheating during, and at the end of, the perstillation. The ordinary electrical immersion heaters are not very adaptable for perstillation[1] owing to overheating any of the elements that may become exposed. Another method of perstillation is of a circulatory type shown in Fig. 4. which is also useful for vacuum work. The heated liquid rises, perstills, cools and then comes down on the other side and in this way circulates. By means of these perstillators liquids may be perstilled without boiling at ordinary atmospheric pressure with temperatures as low as 40–50°.

(*b*) *With Vacuum.*—The designs shown in Figs. 2, 3 and 4 are also suited for vacuum perstillation. The only extra precautions are to add a con-

[1] New designs of immersion heaters are being developed and are under way.

denser and receptacle for catching any vapors that pass the first condenser. Fig. 5 shows a simple but efficient arrangement.

3. Percrystallization. (*a*) *With Easily Crystallizable Substances.*—A 300 cc. collodion container was filled with saturated ammonium sulfate and fanned in a warm room. At once ammonium sulfate crystallized on the outside and blew off like snow.

A similar container was filled with about one-third saturated sodium chloride solution and pervaporated. Only after one-half of the water had pervaporated did crystals of sodium chloride appear on the outside.

(*b*) *With Difficultly Crystallizable Substances.*—A starch digestion mixture containing hydrochloric acid was pervaporated under the same con-

Fig. 4
Circulatory
Perstillator.

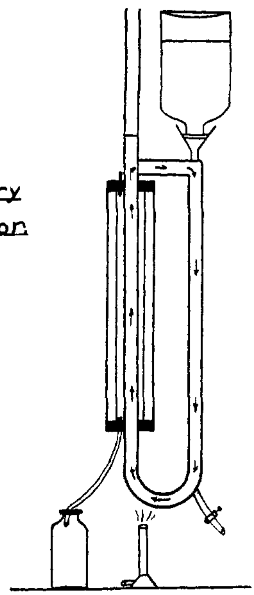
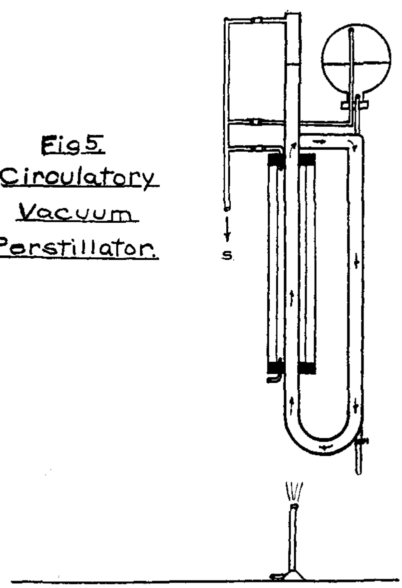


Fig. 5
Circulatory
Vacuum
Perstillator.



ditions as just described. Although the mixture had considerably caramelized, yet a clear practically colorless sugar syrup was obtained. This redissolving of the crystals was due to the extremely hygroscopic maltose which deliquesced.

A protein digestion residue containing strongly hydrochloric acid, histidine and practically black with humin, was pervaporated. White crystals of histidine appeared, but further experimentation was prevented by a leak at a weak spot in the container.

III. Theoretical and Other Considerations.

In seeking an explanation for pervaporation two theories have presented themselves.

(1) That these containers possess a porosity of an extremely fine nature,

allowing vapor molecules to pass freely, but owing to surface tension or some other factors does not allow liquid to pass.

(2) That these membranes are of the nature of gels, and that the outer surface of the gels evaporates and the liquid on the inner surface replenishes, by diffusion, the water thus lost. This theory is in harmony with the fact that ordinary collodion hardens and becomes impermeable when dry, to ordinary dialysis, and also with the fact that all membranes are set or fixed by immersion in water. This fact also indicates that water is a constituent of membranes, either chemically or otherwise, and the rapid drying indicates that this water also has a vapor pressure. Until the solution within a membrane is saturated with a constituent, osmotic pressure seems to prevent any crystallization taking place on the outside. This statement is supported, if not proven, by the fact that percrystallized substances on the outside of the containers will dissolve on adding a little water on the inside. As the crystals are practically dry, and free from mother liquor, percrystallization ought to be useful, not only in many chemical operations heretofore difficult and impossible, but ought to be useful for ordinary crystallization as well. Some crystals, however, seem to have a tendency to puncture the membrane and since different forms of membranes have not been studied, this difficulty perhaps may still be circumvented. It seems probable that other membranes pervaporating other solvents may be found since the usefulness of such a process is now apparent.

IV. Summary.

(1) Collodion and parchment membrane containers permit water to evaporate through the walls as though no membrane were present. This phenomenon is called pervaporation.

(2) Distillation by means of pervaporation is called perstillation, and can be conducted at ordinary atmospheric pressure with low temperatures as well as with vacuum.

(3) When a dialyzable constituent of a liquid within these containers reaches saturation, crystallization usually takes place on the outside. This phenomenon is called percrystallization.

(4) A number of experiments are described which show the possible uses of these phenomena in the arts and sciences. The theoretical considerations of the phenomena are briefly discussed.

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NOTE.

The Reduction of Mercuric Compounds.—In a study of the reduction of mercuric chloride by phosphorous acid and sodium formate, respectively, it was found[1] that concordant velocity constants were obtained

[1] Linhart, *Am. J. Sci.*, 35, 353 (1913); THIS JOURNAL, 37, 70 (1915).