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A Simplified Gas Permeability Apparatus

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Synopsis

A simplified gas permeability apparatus is described which is used in performing the essential functions of more complex conventional designs. An improved diffusion cell clamp is described, and the basic operation of the instrument is outlined. Experimental data are submitted as evidence of the reliability of the instrument.

INTRODUCTION

A simplified gas permeability apparatus was developed for use in an investigation which is described elsewhere.[1] A variety of such, mostly glass units patterned after the original high-vacuum technique employed by Barrer[2,3] have been described in the literature.[4–6] Heretofore these instruments have often tended to be rather complicated devices featuring auxiliary glass circuitry which is used variously to hasten measurements or add to the variety of operations which can be performed within the sealed system. Although reasonable in principle, the practice of attaching additional tubing and connections for the performance of such accessory functions can entail undesirable side effects. The increased number of working parts may invite a more frequent demand for maintenance. The configuration of the apparatus may lead to awkward spatial requirements hampering enclosure of the system in a temperature-controlled environment. Access to the instrument and the manipulation of bulky parts for the purpose of repair or replacement of glassware may also be increasingly difficult. Greater weight and rigidity requirements in a heavily modified apparatus often necessitate a large rack for support. In the development of the presently described permeability apparatus it was considered that benefits in terms of high efficiency and low-maintenance operation which are possible with a simplified design of the instrument outweighed the convenience of accessories.

DESCRIPTION OF THE APPARATUS

Efforts to simplify the apparatus were largely directed toward achieving a more unified structure in which glass circuitry required for basic manipu-

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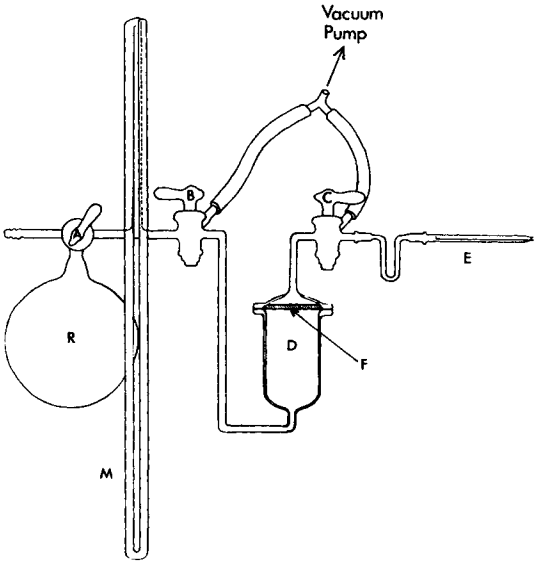

Fig. 1. Simplified gas permeability apparatus.

lations of diffusant would be integrated into the overall design rather than added as distinguishable sections. The completed design shown in Figure 1 (drawn to scale with a manometer height of 50 cm) reveals the routing of all essential circuitry through only two main stopcocks (B and C). A third stopcock (A) is used partly to assist in manipulations of diffusant within the apparatus although its chief function is to admit fresh gas to the system. Each glass joint and fitting is considered as a possible source of pressure leak, and their number is therefore confined to a minimum. Glass joints and stopcocks were carefully hand-ground. In operation the apparatus is suspended in a constant temperature water bath (a 25 × 50 cm aquarium tank was used) with the water level just below the stopcocks. The apparatus is positioned with the gas detector tube (E) and U-trap projecting beyond the edge of the bath at one end of the tank.

Diffusion Cell

The diffusion cell (D) has a lower (pressure) chamber with approximately 200 cm^3 capacity and a small upper (vacuum) chamber separated from each other by the mounted film. (The cell clamp, not shown in Figure 1, is described in the following section.) A sintered-glass diaphragm of medium porosity grade is used at the upper surface of the film (F) for support against the applied gas pressure in the lower chamber. The sintered disk is beveled to fit smoothly into the recess formed by the upper chamber aperture, with its bottom face on an even plane with the ground glass surface of the upper chamber flange. The diaphragm is not sealed to the upper chamber and can be easily removed for replacement and for cleaning the apparatus. The light weight of this porous disk caused no detectable

physical strain on films studied, and any conceivable microscopic deformation occurring with the system at rest would be offset during the experiment by the effect of the applied gas pressure. During a diffusion experiment the upper chamber of the diffusion cell is connected through C and an intervening U-trap (a small Dewar flask used is not shown) to the Pirani tube (E). The trap and the detector tube are each provided with a glass joint to facilitate replacement. Detector tubes operating on the hot-wire principle[7] react strongly to the presence of higher molecular weight vapors indicating pressures substantially greater than the true gas pressure. The miniature liquid nitrogen-cooled U-trap shown was adequate to shield the tube element from the minute quantities of contaminating solvent or monomer vapors which may emanate from recently mounted polymer films or freshly deposited sealing material. Although it was possible to perform diffusion measurements without the use of a trap, its use conveniently obviates the need for lengthy degassing periods. With the diaphragm in place, the internal volume of the upper chamber (with connected trap and detector tube sections) was determined using water as a calibrating liquid. This measuring chamber (approximately 4.0×10^{-2} liter at 25°C) and pressure changes measured within it during the permeability experiment are used to determine the quantity of gas which has entered the upper chamber in a given time. The remaining details of this procedure have been described previously by Meares.[8]

Improved Diffusion Cell Clamp and a Sealing Agent

In work with all-glass diffusion cells some degree of difficulty is often experienced in obtaining what is thought to be a desirable high clamping pressure on the cell flanges in order to promote a gas-tight seal to the polymer film held between. Attempts to obtain high clamping pressure by using rigid clamps resulting in fracture of the cell flanges have contributed strongly to a reputation for glass diffusion cells of being too brittle for practical use. In the present investigation it was considered that high clamping pressures may not be essential and that better advantage might be taken of an improved distribution of clamping pressure around the flanges.

A flexible clamp was constructed from a set of four circular collars machined from a flat sheet of $^1/_8$ in. thick glass fiber-reinforced polyester. The inside diameter of each collar was made slightly larger than the external diameter of the diffusion chamber. A cut was made through each collar so that it could be spread open and passed around glass tubing leading into either end of the diffusion cell. Collars could then be slipped over each chamber to butt up against the protruding cell flanges. The combined thickness of two collars was used to form each half of the cell clamp. Single collars of an equivalent thickness would have been too rigid to pass around the glass tubing. The span from the inside to the outside diameter of each flat collar was twice the horizontal width of the cell flanges leaving space to position four small bolts through holes along the perimeter using

wing nuts to draw the top and bottom halves of the clamp together. Rows of small rubber washers were strung onto each bolt between the clamp halves. On tightening the clamp, the washers are sandwiched between the approaching clamp halves and provide a cushioning resistance to clamping pressure exerted on the opposing cell flanges and the film held between. It is held that the flexible action of this clamp permitting it to conform to slight irregularities in cell dimensions contributed significantly to the more even distribution of clamping pressure around the cell union. A good seal between the film and the ground glass flange surfaces was promoted more efficiently, and no cell breakage problems were encountered. With bolts only moderately tightened by hand, custom-ground cell flanges lightly coated with type T Apiezon grease successfully maintained excellent seals against a variety of polymer films.

In one instance a condition of apparent incompatibility between the grease and a very hard polymer film consistently led to a delayed failure of the seal. From one to several days after an apparently successful seal had been achieved, channels would develop between the grease and the film, leaking air into the system. This problem was completely eliminated by the use of a very thin prime coating of Piccolyte S-115 polyterpene resin (Pennsylvania Industrial Chemical Corporation) applied to the seal area prior to mounting on the greased cell flanges. This resin was compatible with the grease and adheres readily to diverse types of polymers. Tests on several different polymer films with and without the use of this sealant revealed no measurable effect on permeability results.

OPERATION OF THE APPARATUS

The operation of this instrument is reasonably simple despite its highly centralized design. Certain distinctive features result from having relegated all major control functions to only two three-way stopcocks. The broadened role assigned to B and C makes it important to select the most advantageous sequence of stopcock turns for each step in the experiment. The following description is given of a typical procedure.

In preparation for the initial evacuation of the apparatus (with fresh grease in all glass joints and the test film mounted in the diffusion cell) the bores of B and C stopcock plugs are aligned with their respective exits so that B and C are in the all-open position. With A open to the reservoir, the entire instrument may then be evacuated through B and C. In the normal operation of the apparatus, following this initial degassing period, the reservoir and manometer sections are frequently isolated from the diffusion chambers and may be maintained in a state of almost continual evacuation. On the other hand, the supply of gaseous contaminants to the diffusion cell section is periodically renewed through routine substitutions of test films and replacement of sealing materials. Accordingly, preliminary degassing in subsequent experiments was followed by a more drastic evacuation of the diffusion cell and film. For this step,

B is advanced one position in the clockwise direction from its initial (all-open) setting so that the vacuum pump is drawing, simultaneously, from both sides of the film, the U-trap and the electrode. An overnight degassing of the film and seal areas was normally sufficient to reduce gauge reading fluctuations to a negligible level in blank experiments.

In preparation for admission of the gas sample to the lower chamber of the diffusion cell, C is adjusted one-half position in the clockwise direction, isolating the electrode and closing off the vacuum pump from the upper chamber. This is done in order to prevent accidental discharge of gas pressure against the unsupported side of the film during manipulation of the gas within the apparatus. B is then turned one and one-half positions in the counterclockwise direction. As B is turned past the all-open position, loss of vacuum in the lower chamber due to leakage may be momentarily checked for by watching the manometer or noting changes in pitch of the sound from the pump. Gas permeant is then admitted from an external supply to the evacuated reservoir and manometer sections through A which is subsequently returned to its initial position. On this first addition, B is then turned one-half position further, evacuating the two sections. This operation may be repeated several times flushing the sections with fresh gas. On the final addition, A is returned only one-half position in the counterclockwise direction toward its initial setting; and only the manometer section is evacuated. B is then adjusted one-half position in the counterclockwise direction to a new off position. Gas in the reservoir is allowed to equilibrate to the bath temperature and is then bled into the evacuated manometer section by a counterclockwise turn of A.

Stopcock C may now be adjusted to reconnect the U-trap and electrode with the upper chamber of the diffusion cell in isolation from the vacuum pump. C is turned in the counterclockwise direction (two and one-half positions), in the course of which these sections may be given a final brief exposure to the action of the pump. Liquid nitrogen is then added to the trap, and the upper chamber pressure is checked through the gauge reading.

Gas contained in the manometer section is allowed to expand through B (counterclockwise turn) into the lower chamber of the diffusion cell, beginning the experiment. With B temporarily open to the chamber, the applied gas pressure is read from the manometer. B is then turned clockwise to the nearest off position isolating the manometer section. A is subsequently opened from the reservoir to this section, and this part of the apparatus is evacuated through B. The applied gas pressure resulting from an initial charge in the one-liter reservoir was measured. With an initial pressure of 50 cm Hg, the expansion of gas contained in the manometer section yielded approximately 5 cm Hg applied pressure in the lower chamber.

EXPERIMENTAL

Daran 210, a poly(vinylidene chloride) latex, was obtained from Dewey and Almy Chemical Division of W. R. Grace and Company.

Films were prepared by dip-coating the latex onto polyethylene substrate. Films were dried at room temperature rather than baked, after which they were stripped from the substrate and their thickness determined with a Carson Electronic Micrometer, Model M-30 (Carson Micrometer Corporation, Little Falls, New Jersey).

RESULTS AND CONCLUSIONS

The presently described apparatus has been used successfully in investigations of permeability on a variety of polymer films.[1] Good agreement with the results of other investigators was obtained.

The reliability of the apparatus was further assessed through measurements of very low permeabilities. An unusually low permeability film was prepared by drying poly(vinylidene chloride) latex at room temperature. In a typical experiment with this film the measured oxygen permeability at 25°C was $4.6_6 \times 10^{-14}$ cm³ (STP) mm/cm²-sec-cm Hg.

The apparatus was found to be extremely gas-tight and dependable in operation. These attributes, in combination with the small size of the diffusion cell upper chamber, enabled sensitive measurements of very low rates of permeation.

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