JOURNAL OF MATERIALS SCIENCE 11 (1976) 1187–1199

Microporous glasses for reverse osmosis

P. W. MCMILLAN, C. E. MATTHEWS
Department of Physics, University of Warwick, Coventry, UK

The preparation, heat-treatment and leaching of phase separable borosilicate glasses which are of interest as possible semipermeable membranes for reverse osmosis applications are described. It is shown that the kinetics of phase separation are consistent with spinodal decomposition being the phase separation mechanism but this is not a rigorous conclusion. Characterization of the porous glass by electron microscopy and by a gas adsorption balance suggested the presence of fine scale features not resolved by electron microscopy. The microporous glass was shown to function as a reverse osmosis membrane although changes in the performance indicated the need for improved glass compositions and heat-treatment procedures.

1. Introduction

There is considerable interest in improved methods for the production of fresh water from the sea and one of the most promising techniques is reverse osmosis desalination. In this, sea water contained by a suitable semipermeable membrane, is subjected to a pressure higher than the osmotic pressure and desalinated water is thereby "pumped" through the membrane. Reverse osmosis is economical both with regard to space and power requirements and hence the motivation for the development of improved systems.

A key area in which improvement might be achieved concerns the semipermeable membrane itself. Cellulose acetate membranes have been used successfully in many reverse osmosis applications but several difficulties have become apparent. Under the necessary high operating pressures, permanent compaction of the membrane material can occur leading to unacceptable reduction of throughput. Degradation of the membrane by hydrolysis results in impairment of performance and biological attack can cause complete breakdown under certain conditions. These problems can be overcome by operating at reduced pressures, by acidifying the water and by adding biocides but these measures are generally undesirable since they increase the size of plant for a given input and detract from the inherent simplicity of operation.

It has been known for many years [1] that microporous materials can be prepared by the leaching of phase-separated glasses and the possible application of these as semipermeable membranes for reverse osmosis applications has been the subject of a previous investigation [2]. The latter gave support to the view that a glass membrane may not be subject to hydrolytic degradation or to compaction effects. In addition, it is thought unlikely that glass would be susceptible to biological attack.

Amorphous phase-separation can occur in a large number of glass systems but in order to produce a microporous material certain requirements have to be fulfilled. First both phases must be interconnected and secondly, one phase must be highly soluble and the other relatively insoluble in a suitable reagent to allow selective leaching to occur. The degree of interconnectivity of the two glass phases is dependent on the nature of the phase-separation process. Nucleation and growth of the second phase gives, in the early stages, isolated spherical particles but when the volume fraction of this phase becomes sufficiently large, adjacent spheres may touch and partially coalesce resulting in an interconnected morphology. In spinodal decomposition [3] an interconnected morphology develops in the early stages.

The necessary differentiation between the two phases with regard to their solubilities is achieved by proper selection of the initial glass composition and it has been found that compositions in the alkali metal oxide–boric oxide–silica system are particularly useful. In this case suitable heat-treatment causes separation into two interconnected phases one of which is almost pure silica (~ 96% SiO_2) and the other of which is substantially an alkali borate glass. The latter is soluble in dilute acid whereas the silica phase is not.

The objectives of the investigation described in the present paper were to study the preparation of phase-separable borosilicate glasses, to explore the effects of heat-treatment upon their microstructures, to characterize the microstructures of the leached glasses by high resolution electron microscopy and gas adsorption techniques and finally, to assess the possible usefulness of the microporous glasses as membranes for reverse osmosis desalination.

2. Glass compositions and preparation

Glasses 1 to 5 in Table I were selected for preliminary investigation since it was expected that these would be single-phase in the molten state, would remain so during rapid cooling but could be induced to phase-separate by subsequent heat-treatment. The raw materials used for glass preparation were sodium carbonate, lithium carbonate, borax and anhydrous boric oxide. After thorough mixing, the materials were melted at temperatures of 1000 to 1200° C in platinum crucibles for 3 to 4 days. The temperature chosen for a particular glass depended on the viscosity of the melt but was kept as low as possible to minimize volatization losses.

TABLE I Compositions of the experimental glasses (wt%)

Glass no.	SiO_2	B_2O_3	Na_2O	Li_2O	Al_2O_3
1	65	31	4	–	–
2	65	26	9	–	–
3	70	21.5	8.5	–	–
4	68	29	–	3	–
5	60	30.5	9.5	–	–
6	56.2	32.4	8.4	–	3
7	57.5	31.4	9.1	–	2

Apart from glass 1, the glasses appeared to be homogeneous to visual inspection but subsequent optical and electron microscopy suggested the need for improved homogeneity. Later melts were, therefore, prepared at 1450° C with continuous stirring using a motor driven platinum stirrer. To compensate for the volatilization losses, additional boric oxide, amounting to one twentieth of the normal boric oxide content, was added.

Glass 5 prepared in this way showed considerably improved homogeneity as compared with glass prepared by the earlier technique.

Following the initial studies it was thought desirable to modify the glass compositions by the inclusion of a small proportion of aluminium oxide. The object was to decrease the rate of phase-separation by increasing the viscosity of the glasses. This was considered advantageous because it would allow the kinetics of phase-separation to be studied more readily and furthermore, because it would render the process more controllable and minimize phase-separation during the cooling of the glass.

Glass 6 (Table I) proved to be too viscous at the melting temperature and, therefore, glass 7 containing 2 wt% Al_2O_3 was prepared. This glass could be refined satisfactorily and produced in a homogeneous form.

Specimens for subsequent examination were prepared either by casting the molten glass into blocks or by pressing the glass into a thin layer between cooled steel plates. The latter technique ensured rapid quenching from the molten state and this minimized the possibility of premature phase-separation. For the reverse osmosis experiments hollow glass fibres about 0.5 to 1 mm external diameter and having wall thickness of about 80 to 130 μm were prepared from the molten glass by a drawing technique.

Heat-treatment of specimens for subsequent examination was generally in the range 500 to 700° C with durations of 1 to 40 h. Full details of the heat-treatments employed are given in subsequent sections of this paper.

3. Electron microscope studies

High resolution transmission electron microscopy of thin sections of the phase-separated glasses was utilized as a method likely to reveal the morphology of phase-separation enabling the kinetics of the process to be followed.

3.1. Techniques

Several methods of preparing the necessary thin (~ 10^3 Å) sections were investigated. The chemical thinning of 250 μm slices of glass using an HF-HCl etchant was unsatisfactory. The preparation of thin sections by a grinding and polishing technique proved impractical and while ion beam thinning by bombardment with argon ions gave large thin areas, it was found that the process appeared to alter the phase-separation microstructure and this technique was, therefore, abandoned.

The most successful technique and the one that was finally adopted, made use of a fine powder prepared by crushing in a percussion mortar. It was found that the fine powder could be leached to remove the soluble phase in distilled water and after drying, small particles could be mounted on electron microscope grids. This method gave highly satisfactory results since the leaching process ensured that the silica skeleton was clearly delineated in the electron microscope.

For the majority of the studies, the glass specimens were examined using a Hitachi 125 kV high resolution microscope.

3.2. Results and discussion

3.2.1. Preliminary observations on glass 3

Specimens of cast glass 3 developed a well-defined interconnected two-phase structure after suitable heat-treatment as shown by the electron micrograph of material heat-treated at 630° C for 12 h (Fig. 1). The lithia-containing glass 4, however, developed a droplet microstructure rather than the desired interconnected structure even after heat-treatment for prolonged periods at 650° C (Fig. 2).

A more detailed investigation of the effects of heat-treatment on the microstructure of glass 3 was undertaken and the effects of temperature of heat-treatment in the range 500 to 700° C for a fixed duration of 8 h and of duration of heat-treatment at a fixed temperature of 573° C were studied. Figs. 3 to 5 illustrate the effects of heat-

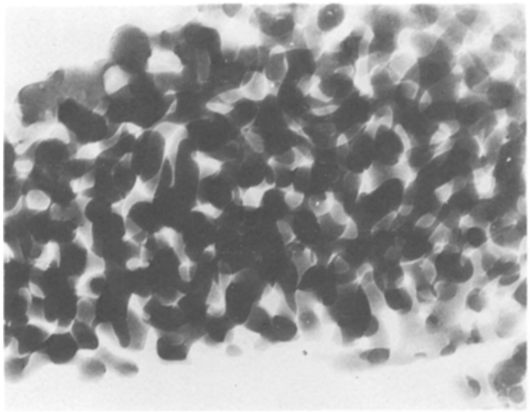

Figure 1 Electron micrograph of leached glass 3 (heat-treated 630° C/12 h), × 17 500.

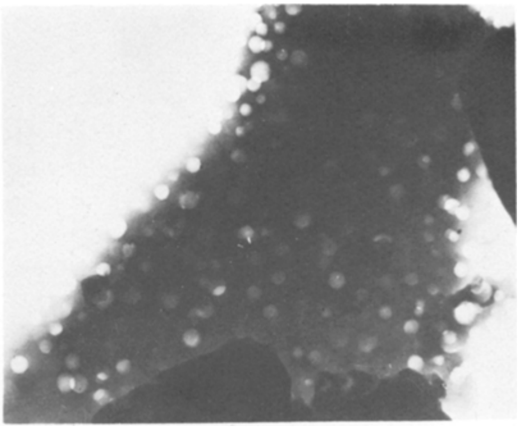

Figure 2 Electron micrograph of leached glass 4 (heat-treated 650° C/38 h), × 32 000.

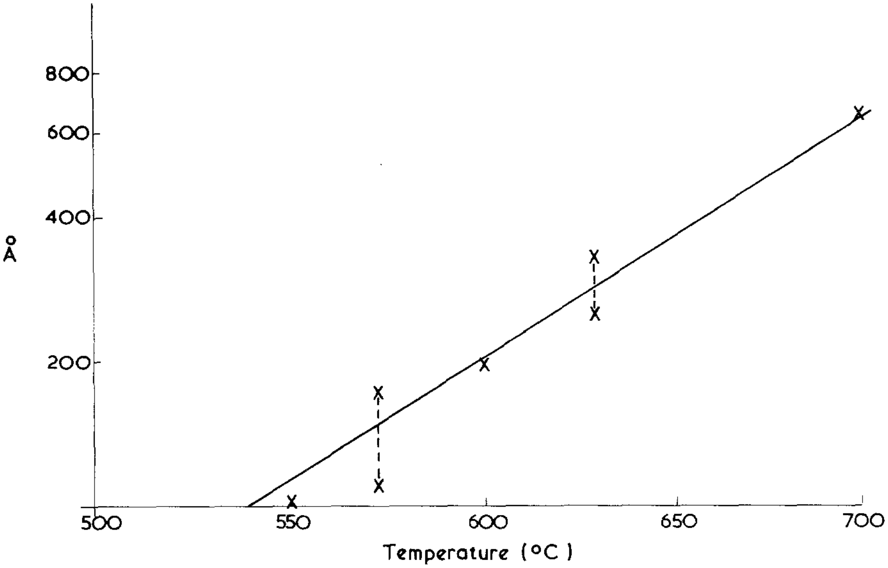

Figure 3 Pore diameter as a function of heat-treatment temperature (duration 8 h) for cast glass 3.

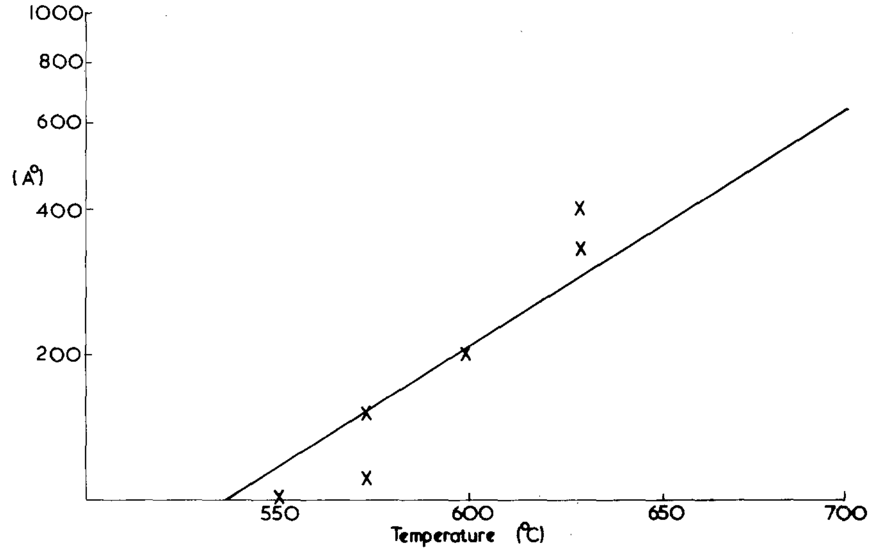

Figure 4 Diameter of silica skeleton as a function of heat-treatment temperature (duration 8 h) for cast glass 3.

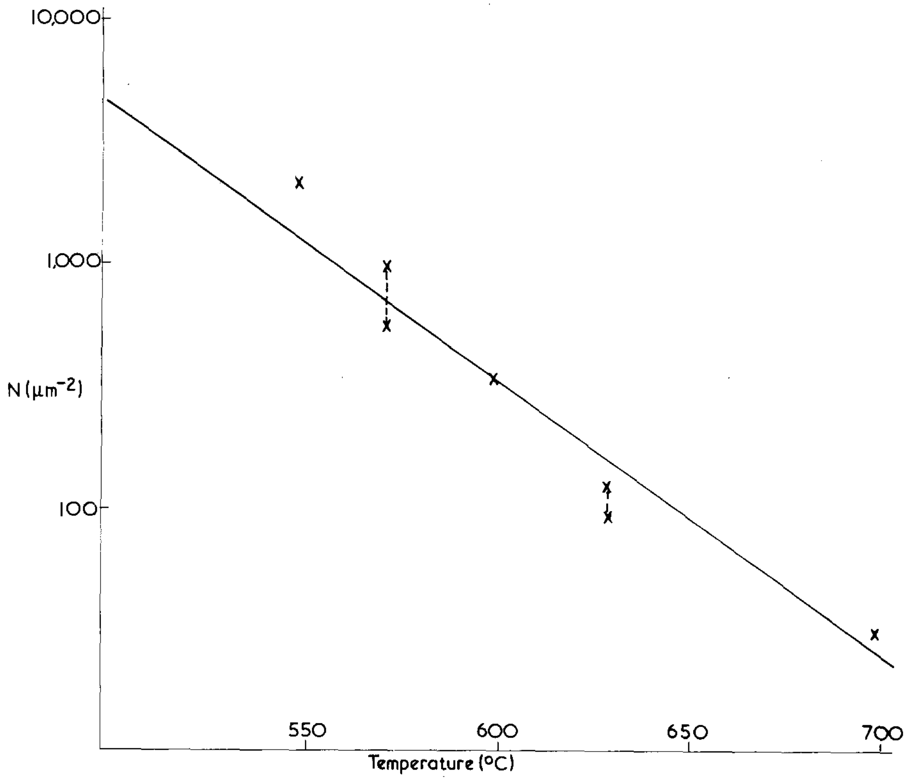

Figure 5 Number of pores per unit area as a function of heat-treatment temperature (duration 8 h) for cast glass 3.

treatment on mean diameters of pores, mean diameter of silica skeleton and number of pores per unit area respectively. These data were derived from electron micrographs of thin sections of the leached glass using standard stereological techniques. Results, obtained in the same way, for the influence of duration of heat-treatment upon the same parameters are given in Figs. 6 to 8.

It is seen that the mean pore diameter and silica skeleton diameter increase and the number of pores per unit area decrease exponentially with heat-treatment temperature. This is consistent

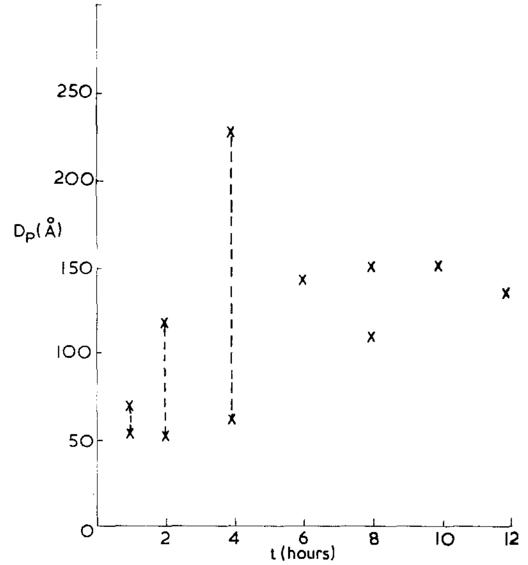

Figure 6 Pore diameter as a function of duration of heat-treatment at 573° C for cast glass 3.

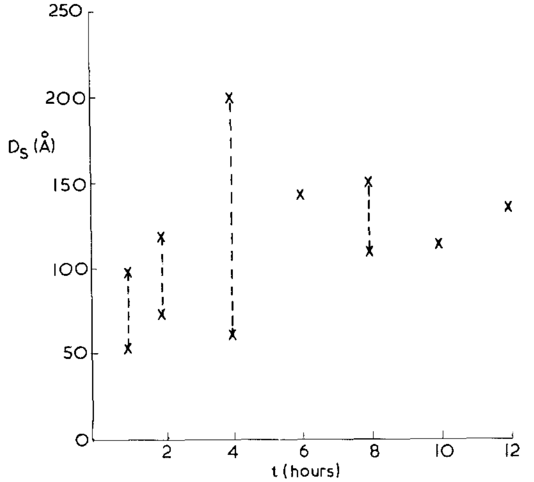

Figure 7 Diameter of silica skeleton as a function of duration of heat-treatment at 573° C for cast glass 3.

with spinodal decomposition rather than nucleation and growth being the mechanism of phase-separation [3, 4]. The occurrence of the interconnected phase-separation microstructure rather than the development of discrete globules may also suggest that spinodal decomposition is responsible for phase separation though a nucleation and growth process is not unequivocally ruled out [5].

The use of cast glass, which was therefore cooled relatively slowly, as the starting material was a disadvantage since it could not be guaranteed that incipient phase-separation prior to heat-

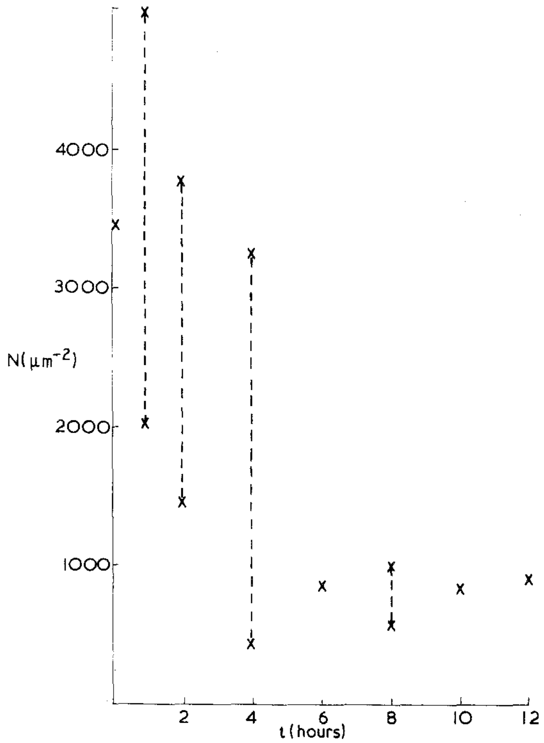

Figure 8 Number of pores per unit area as a function of duration of heat-treatment at 573° C for cast glass 3.

treatment had not occurred. Thus the microstructural changes observed could have been associated with the coarsening of microstructure already present.

3.2.2. Investigation of the microstructure of glass 7

In the light of the earlier results, it was decided to use only glass specimens that had been prepared by the rapid quenching method. It was expected that these would be free from microphase separation at the commencement of the heat-treatment processes and electron microscopy of thin sections of quenched glass 7 gave confirmation of this.

The kinetics of phase-separation in the glass were studied by investigating the effects of isothermal heat-treatment at temperatures in the range 500 to 600° C. From electron micrographs of thin sections values of λ, the mean spacing between structural elements, were derived. This parameter was chosen as being the most convenient to characterize the microstructure and to enable theoretical ideas on phase-separation kinetics to be examined. It is useful to note that the mean pore diameter is about 40% of the value of λ.

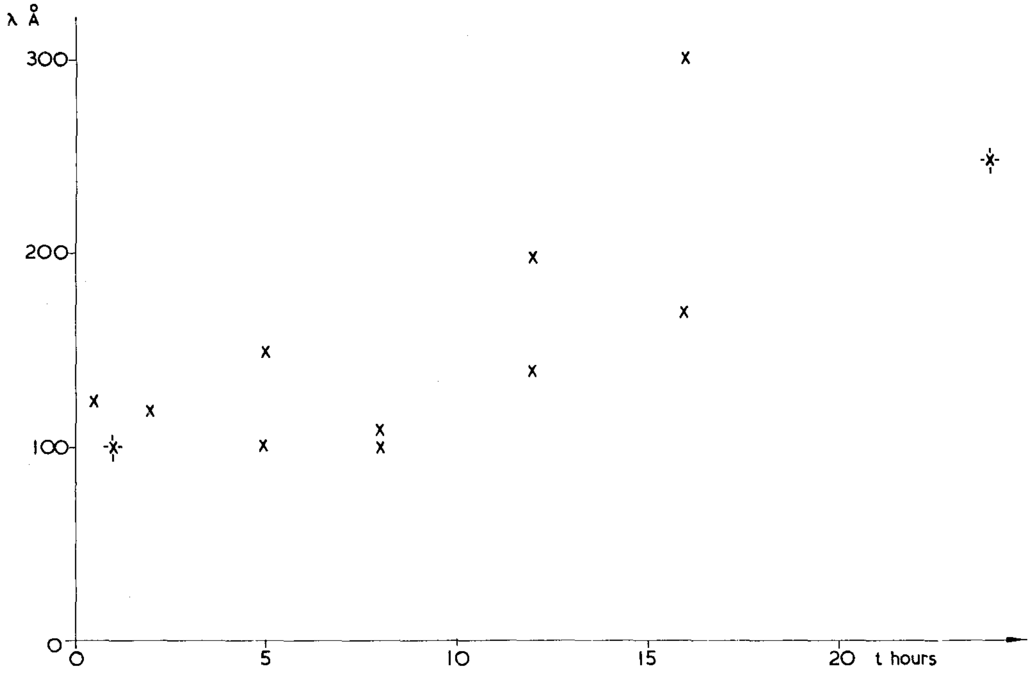

Figure 9 Dependence of λ on duration of heat-treatment at 500° C for quenched glass 7.

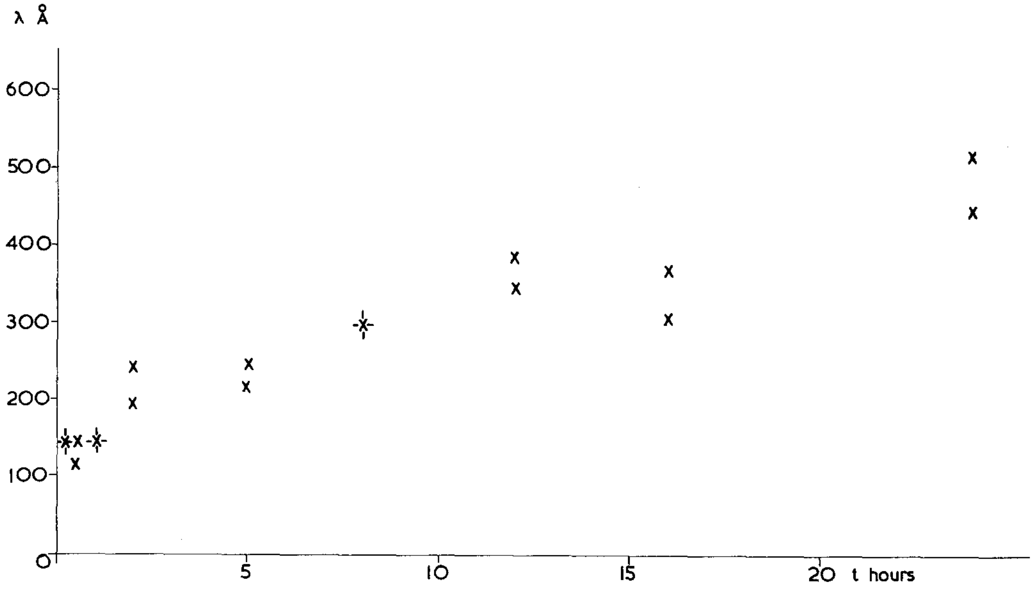

Figure 10 Dependence of λ on duration of heat-treatment at 550° C for quenched glass 7.

Figs. 9 to 11 show λ as a function of heat-treatment duration at temperatures of 500, 550 and 600° C respectively. It will be noted that at all temperatures λ increases with increased duration of heat-treatment, i.e. coarsening of the microstructure is taking place.

For glass that has phase-separated by either the nucleation and growth process or by spinodal decomposition, the particles size will increase with time in accordance with a diffusion limited process such that:

$$\lambda^3 = Kt \qquad (1)$$

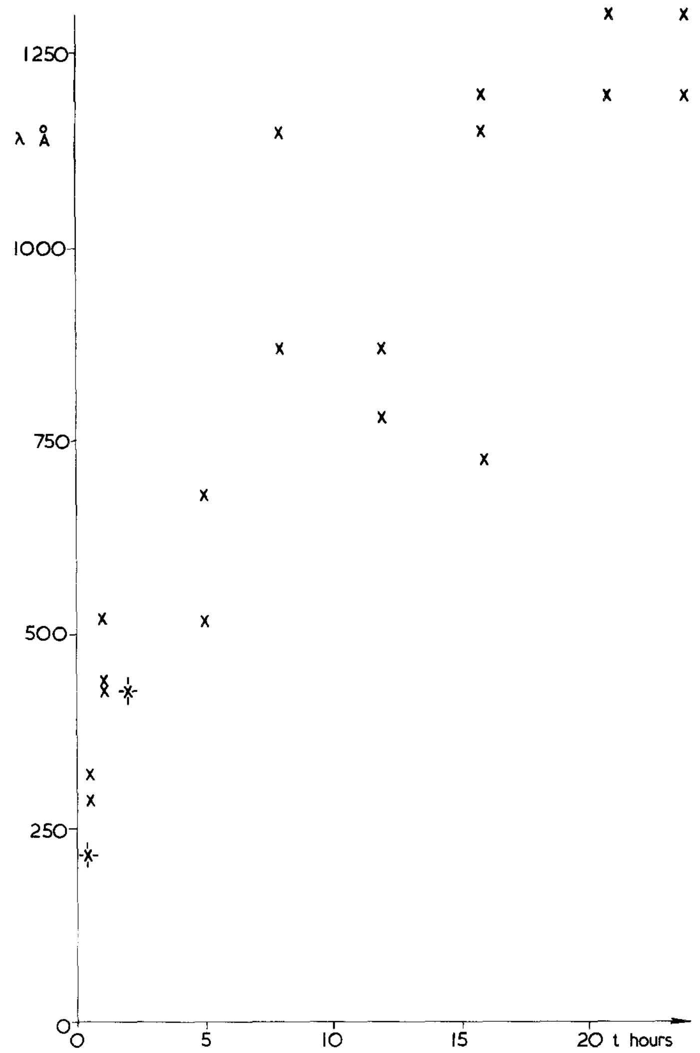

Figure 11 Dependence of λ on duration of heat-treatment at 600° C for quenched glass 7.

where K is a constant.

For spinodal decomposition the expression is:

$$\lambda^3 - \lambda_0^3 = B(t - t_0) \qquad (2)$$

As shown in Fig. 12, the relationship between λ and $t^{1/3}$ is a straight line as predicted in Equation 2.

The rate constant, B, is an Arrhenius function of temperature and a plot of log B versus reciprocal of absolute temperature yields a straight line as shown in Fig. 13. From the slope of this line the value of the activation energy of diffusion is 17 kcal mol^{-1}. This relatively low activation energy is close to that for sodium ion diffusion in glasses, as determined from electrical conductivity measurements, and is much lower than that for viscous flow. This may suggest that the coarsening of the phase-separated microstructure during prolonged heat-treatment is controlled by diffusion of alkali metal ions rather than by the transport of network-forming anionic groups.

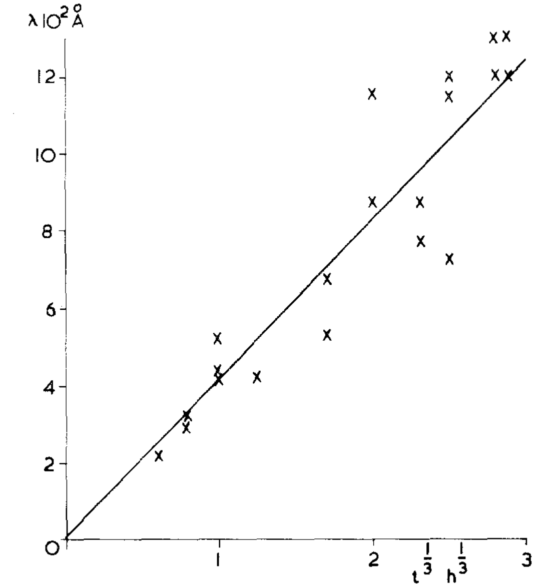

Figure 12 Relationship between λ and $t^{1/3}$ for quenched glass 7 heat-treated at 600° C.

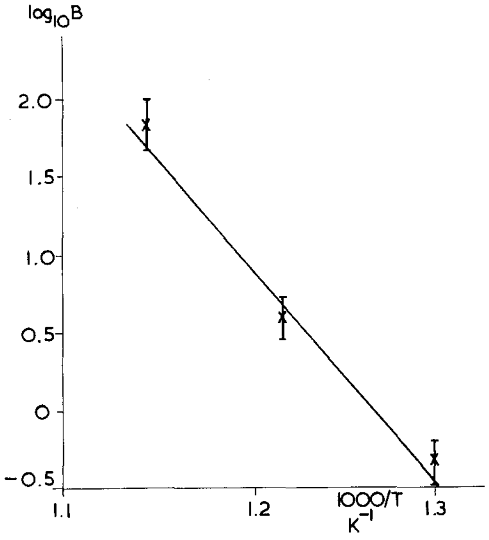

Figure 13 Rate constant B as a function of reciprocal temperature for quenched glass 7.

For times less than t_0, spinodal decomposition theory predicts that λ remains constant at λ_0 and that λ_0 varies with temperature in accordance with:

$$\frac{1}{\lambda_0^2} = \mathrm{K}(T_s - T) \qquad (3)$$

where T_s is the spinodal temperature. Fig. 14 shows that this relationship is obeyed approximately and hence a value for T_s of 640° C can be deduced.

4. Characterization of microporous glasses by gas adsorption studies

4.1. Techniques

Preliminary investigation was undertaken of a method using apparatus which depended on volumetric methods to determine the nitrogen adsorption isotherm. The method was found to be inaccurate and a direct weighing adsorption

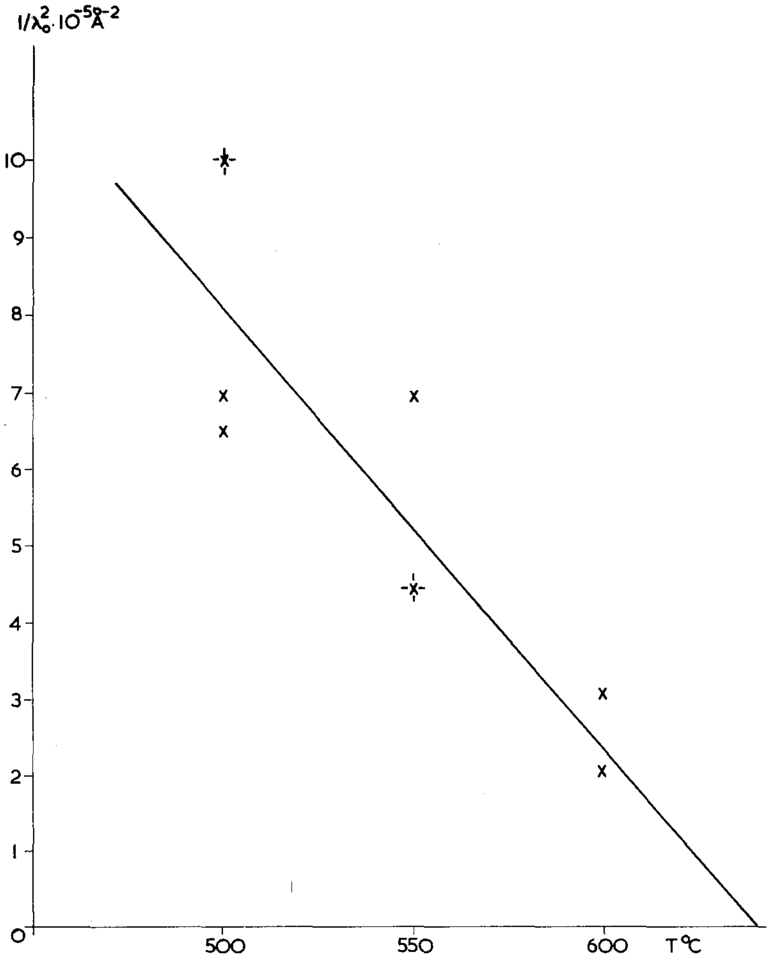

Figure 14 Relationship between λ and heat-treatment temperature for quenched glass 7.

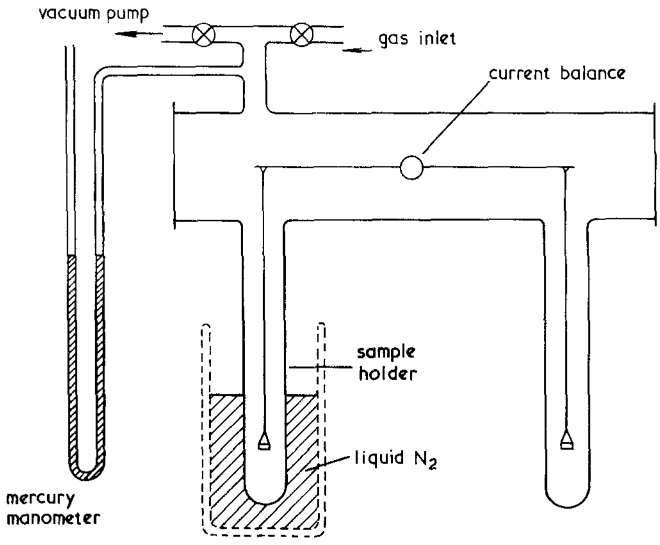

Figure 15 The gas adsorption balance.

balance of the general design illustrated in Fig. 15 was, therefore, constructed.

The balance comprised a tungsten wire beam attached to an ammeter movement. A polythene pan suspended from one arm of the beam contained the specimen of powdered porous glass and a similar counterbalancing pan was attached to the other arm. The increase in weight of the glass specimen caused by nitrogen adsorption was determined by measuring the current required to restore the ammeter movement to its zero position. The sensitivity of the balance was 2.2 mA mg^{-1} and the precision ± 0.3 mA. This equipment proved to give accurate and reliable measurements of adsorption isotherms.

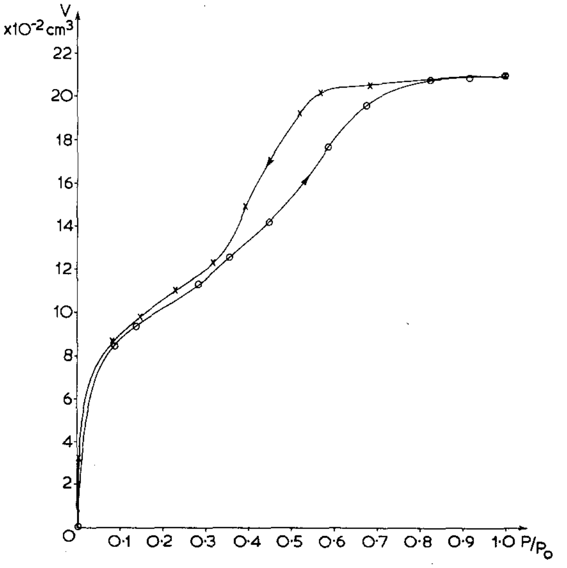

Figure 16 Adsorption and desorption curves for glass 7.

Measurements were made on glass 7 that had been heat-treated for periods of 5 h at 500, 550 and 600° C before leaching (Fig. 16).

Pore sizes were derived by two different methods.

(1) Applying the BET equation [6] to the adsorption curve, the surface area A was obtained. Then if V is the volume of gas adsorbed, the average pore radius $\bar{R}$ is given by:

$$\bar{R} = \frac{2V}{A}. \tag{4}$$

(2) Using a numerical difference analysis [7] a pore size distribution $\Delta V/\Delta R$ versus R was obtained from the desorption curve.

4.2. Results and discussion

The results of the gas adsorption studies are summarized in Table II. Fig. 17 shows the pore size distribution derived from the desorption curve for glass 7 heat-treated at 500° C for 5 h. The well-defined peak value for $\bar{D} = 30$ Å is in reasonable agreement with the value of 37 Å derived from the adsorption measurements. These values were, however, significantly smaller than that deduced from electron microscopy (~ 60 Å).

Fig. 18 shows the pore size distribution for the glass heat-treated at 550° C for 5 h. The distribution curve showed more than one peak and thus it is difficult to assign an unambiguous value for $\bar{D}$. The two main peaks correspond to pore diameters of 44 and 15 Å. The former is in reasonable agreement with the value derived from the adsorption curve but it is again very much smaller than the

TABLE II Results of pore size determinations on leached specimens of glass 7

Heat-treatment	Adsorption measurements		Desorption measurements	Electron microscopy mean pore diameter, D (Å)
	Surface area, A ($m^2 g^{-1}$)	Mean pore diameter, D (Å)	Mean pore diameter, D (Å)	
500° C/5 h	228	37	30	~60
550° C/5 h	250	37	44 and 15	~300
600° C/5 h	275	27	–	~400

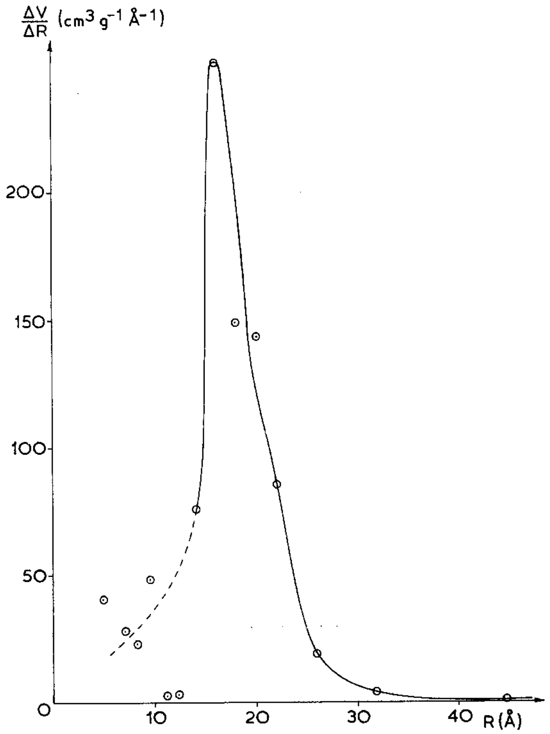

Figure 17 Pore radius distribution curve for glass 7 heat-treated at 500° C for 5 h.

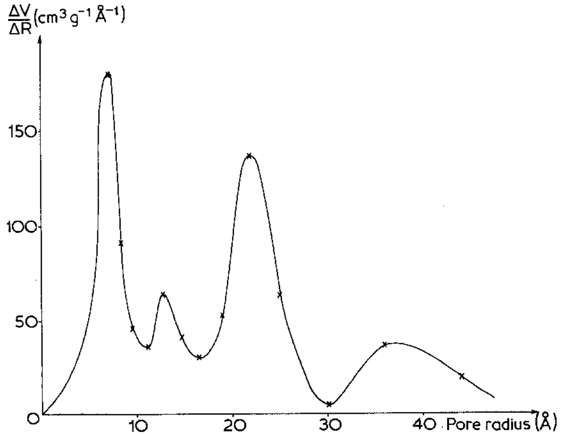

Figure 18 Pore radius distribution curve for glass 7 heat-treated at 550° C for 5 h.

value of ~ 300 Å suggested by electron microscopy. In the case of glass heat-treated at 600° C for 5 h, it was not possible to obtain meaningful results from the desorption measurements but the value for $\bar{D}$ of 27 Å derived from the adsorption curve was very much smaller than the pore size indicated by electron microscopy.

It is considered that the differences in average pore size found by the two methods of microscopy and gas adsorption are possibly due to small irregularities on the walls of the pores or to "substructure" within the pores, neither of which would be resolved by the electron microscope employed. Thus the total surface area available for adsorption may be considerably greater, for a given volume adsorbed, than would be suggested by electron microscopy and the apparent value of $\bar{D}$ would be decreased. A similar effect has been reported by Zhdanov [8]. Clearly, there is a need for further work on this aspect.

5. Reverse osmosis studies

5.1. Equipment and specimens

The equipment shown schematically in Fig. 19 was constructed using wherever possible high grade stainless steel piping and components to minimize corrosion problems. The design of the reverse osmosis cell is given in Fig. 20 and the glass membrane took the form of a hollow fibre sealed at one end into a stainless steel plug using an epoxy resin, the other end of the fibre being flame-sealed prior to mounting.

The hollow fibres were prepared from the molten glass by a drawing technique and after suitable lengths had been heat-treated under specified conditions leaching was carried out by immersing overnight in a solution of 3 N HCl saturated with NH_4Cl. Flame-sealing of the "closed" end of the fibre was carried out prior to leaching since attempts to seal the leached glass resulted in frothing. The dimensions of specimens used for reverse osmosis are given in Table III.

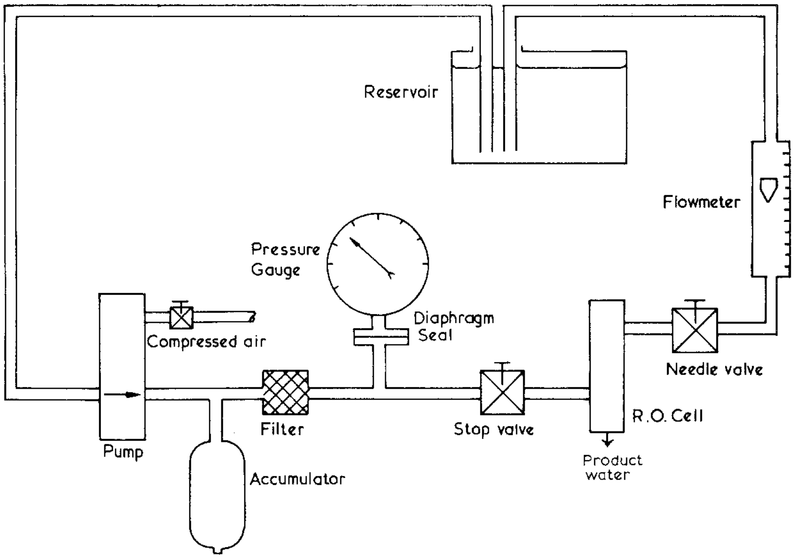

Figure 19 The experimental reverse osmosis equipment.

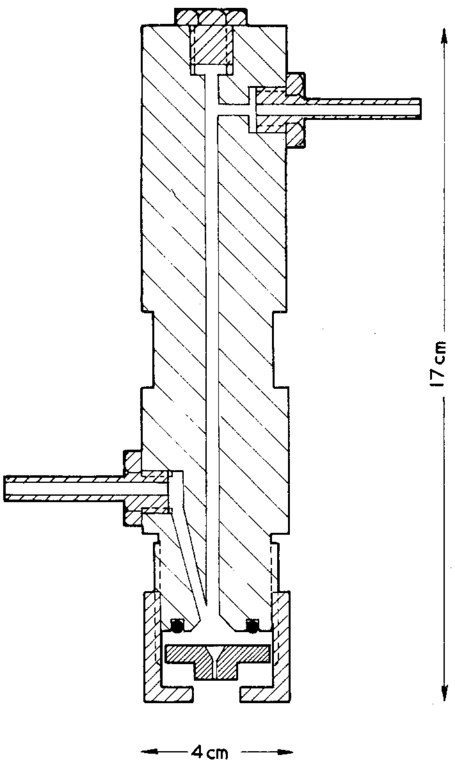

Figure 20 The reverse osmosis test cell.

TABLE III Dimensions of the reverse osmosis specimens

	Heat-treatment	
	500° C/5 h	600° C/5 h
External diameter (μm)	550	920
Internal diameter (μm)	370	680
Wall thickness (μm)	90	120
Length (cm)	9.8	6.1
Surface area (cm^2)	1.4	1.5
Mean pore diameter (Å) (by transmission electron microscopy)	60	400

For the determination of salt concentration in the product solution, it was found that the best method was to measure the electrical conductivity of the product water. For this purpose, conductivity cells made from capillary tubing were employed and the results were compensated to allow for changes in ambient temperature. The rejection S was derived from:

$$S = 1 - \frac{R_s}{R_p} \tag{5}$$

where R_s is the resistance of the feed solution and R_p is the resistance of the product solution.

The product output rate, Q, was found by measuring the time taken for the conductivity cell to fill, having previously determined its internal volume.

In addition to salt rejection rate, S, and product output rate, Q, a third parameter, the permeability, K, was of interest. The latter two parameters are related by the expression:

$$Q = K\frac{A}{t}(\Delta p - \pi) \tag{6}$$

giving

$$K = \frac{Qt}{A(\Delta p - \pi)} \qquad (7)$$

where Δp = gauge pressure ($\mathrm{kg\,m^{-2}}$), π = osmotic pressure ($\mathrm{kg\,m^{-2}}$), A = surface area of membrane ($\mathrm{m^2}$), t = wall thickness of membrane (μm).

For the reverse osmosis experiments it was decided to employ a solution of sodium benzoate as the feed solution rather than sodium chloride solution. The aim was to inhibit the formation of ferrous hydroxide in the system. However, the advantage hoped for was not fully achieved since fairly rapid blocking of the filter still occurred. The solution used had a concentration of 2% w/v and the pH was found to be about 7. The osmotic pressure, π, was calculated as about $60\,\mathrm{kg\,m^{-2}}$ using the van't Hoff equation.

5.2. Results and discussion

The results obtained for a membrane produced from glass 7 heat-treated at 500° C for 5 h are summarised in Table IV. For this specimen, the rejection rate, S, appeared constant for a given value of Δp throughout the nine day test period but the values of Q and K apparently increased.

Table V summarizes the results for a membrane produced from glass 7 heat-treated at 600° C for 5 h. This specimen gave a significantly lower salt rejection rate than the previous one and also the rejection rate decreased for a given gauge pressure, Δp, during the period of test. Increases in the values of Q and K were also observed with increased duration of testing.

TABLE IV Results of reverse osmosis measurements for glass 7 heat-treated at 500° C/5 h

ΔP ($\mathrm{kg\,cm^{-2}}$)	S (%)	Q ($\mu\mathrm{l\,h^{-1}}$)	K ($10^{-11}\,\mathrm{m^2\,h^{-1}}$ $(\mathrm{kg\,cm^{-2}})^{-1}$)	Days in test cell
50	61 ± 5	98	12.7	2
40	56 ± 6	95	16.0	3
70	62 ± 5	200	17.8	4
50	60 ± 6	154	20.0	4
50	61 ± 5	235	30.0	9
100	67 ± 5	490	30.0	9

TABLE V Results of reverse osmosis measurements for glass 7 heat-treated at 600° C/5 h

ΔP ($\mathrm{kg\,cm^{-2}}$)	S (%)	Q ($\mu\mathrm{l\,h^{-1}}$)	K ($10^{-10}\,\mathrm{m^2\,h^{-1}}$ $(\mathrm{kg\,cm^{-2}})^{-1}$)	Days in test cell
70	48 ± 7	57	7.1	1
70	44 ± 8	90	11.2	6
100	43 ± 8	120	10.2	7
60	39 ± 9	98	14.5	8
30	29 ± 10	52.5	17.5	11
70	31 ± 10	150	19.0	13
70	30 ± 10	155	19.0	14
100	28 ± 10	180	15.3	14

The lower salt rejection rate found for the second specimen is consistent with the larger pore size as indicated by the results of electron microscopy. It is possible, however, that the "true" pore size is very much smaller than the electron microscope results suggest since, as discussed earlier, the pore size determined by gas adsorption differs markedly from the value derived from electron microscopy.

The decrease of rejection rate for the second specimen during the test period suggests that further leaching of the glass membrane was occurring during exposure to the test conditions, possibly resulting in increase of the average pore size.

6. Conclusions

For the preparation of microporous glass by the leaching of phase separated borosilicate glasses, care is needed to ensure that the starting glass is very homogeneous if a material having a uniform microstructure is to be prepared. The inclusion of a small proportion of aluminium oxide in the glass composition is advantageous in preventing premature phase separation and in enabling better control of the phase separation process.

The microstructural parameters of the phase separated glass are related to the temperature and duration of heat-treatment in a predictable manner that is consistent with spinodal decomposition being the phase separation mechanism. However, insufficient evidence is available for this to be regarded as a rigorous conclusion. The results suggested that the coarsening of the microstructure which occurs during prolonged heat-treatment was controlled by the diffusion of alkali metal ions rather than by the transport of network forming anionic groups.

For the complete characterization of a porous glass membrane, electron microscopy alone is inadequate because gas adsorption measurements show that the surface area of the membrane is considerably larger than would be anticipated from electron microscopy studies. This suggests the presence of surface features on the walls of the pores, such as fissures or very small diameter pores, or of "sub-structure" within the pores. These features are presumed to be incapable of resolution by the available electron microscope.

From the limited data obtained on reverse osmosis performance, the salt rejection appears to be determined by the pore size but further research on this aspect is necessary. It is also clear that to obtain a satisfactory long term performance, modifications of the glass composition and heat-treatment process are necessary since there was evidence that leaching of the membranes continued to occur during the reverse osmosis tests.

Acknowledgments

This work has been carried out with the support of Procurement Executive, Ministry of Defence. The authors wish to thank Mr J. M. Taylor, Central Dockyard Laboratory for helpful discussions.

References

1. H. P. HOOD and M. E. NORDBERG, US Patent 2, 106, 744 (1938).
2. S. V. PHILLIPS, D. S. CROZIER, P. W. MCMILLAN and J. McC. TAYLOR, *Desalination* **14** (1974) 209.
3. J. W. CAHN and R. J. CHARLES, *Phys. Chem. Glasses* **6** (1965) 181.
4. J. W. CAHN, *J. Chem. Phys.* **42** (1965) 93.
5. W. HALLER, *ibid* **42** (1965) 686.
6. S. BRUNAUER, P. H. EMMETT and E. TELLER, *J. Amer. Chem. Soc.* **60** (1938) 309.
7. C. ORR and J. DALLA VALLE, "Fine Particle Measurement" (MacMillan, London, 1959) p. 270.
8. S. P. ZHADANOV, *Dokl. Akad. Nauk. U.S.S.R.* **82** (1952) 281.

Received 29 December 1975 and accepted 9 February 1976.