SIMPLE BUT INFORMATIVE EXPERIMENTS ON A PLAIN SEPARATOR FOR LEAD–ACID BATTERIES

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Summary

The mass transport properties of separators are deducible from the properties of the solution in the pores provided that the thickness, porosity, and tortuosity of the separator are known. Unexpected difficulties were encountered in directly measuring thickness, and an indirect method based on the liquid-filled volume of the separator was used. The latter required the amount of surface liquid held externally in the rough surface topography of the separator to be estimated. This was achieved by diffusion ingress experiments and the value obtained was confirmed by Talysurf measurements. The diffusion ingress experiments, a previously untried technique, also allowed an estimate of the tortuosity to be made and the good agreement between the experimental data and a theoretical model established that all the pores in Darak Armorib AR 60 had essentially the same tortuosity.

1. Introduction

Separator materials are usually inert to the ion-conducting liquid contained within their pores. In consequence, the properties of the ion-conducting liquid within the separator are identical with those of bulk liquid. Mass transport is changed only by the 'obstacle' effect of the separator material which causes ions to follow tortuous paths. Equations for mass transport in bulk solution may be made applicable to separators by multiplying all concentration terms by the porosity of the separator and by dividing all mobility terms by the square of the tortuosity [1]. The porosity, V, is the fraction of the total volume of the separator occupied by the ion-conducting liquid, and tortuosity is pore or ionic path length divided by separator thickness. Thus, the specific conductivity of an electrolyte solution, κ, where

$$\kappa = F(c_+ u_+ + c_- u_-) \tag{1}$$

is readily converted into the specific conductance of a separator, $\bar{\kappa}$ where

$$\bar{\kappa} = F(c_+ u_+ + c_- u_-)V/\theta^2 \tag{2}$$

c_+ and c_- are concentrations of ions in g equiv. cm^{-3}, u_+ and u_- are ionic mobilities in cm s^{-1} under a potential gradient of 1 V cm^{-1}, F is the Faraday, V is as given above and θ is the pore length/separator thickness ratio.

Combining eqns. (1) and (2);

$$\frac{\bar{\kappa}}{\kappa} = \frac{V}{\theta^2} \tag{3}$$

Diffusion may be treated similarly [1];

$$\frac{\bar{D}}{D} = \frac{V}{\theta^2} \tag{4}$$

where $\bar{D}$ and D are the diffusion coefficients appropriate to the separator and bulk solution, respectively.

Clearly porosity and tortuosity are important parameters of a separator since knowledge of them enables separator properties to be calculated from the properties of the bulk solution.

Measurement of porosity is more difficult than is often realised

$$V = (Al - v_p)/Al \tag{5}$$

where v_p cm is the volume of the separator material and A cm^2 and l cm are the geometric area and thickness of the piece of separator, respectively. v_p is readily determined from weight and density, area is also easily determined, but as will be shown, measurement of the thickness presents problems. An alternative is to fill the separator with water and determine its total volume by weighing the water-filled separator in air, W_A g and water W_W g. Then

$$Al = (W_A - W_W)/\rho \tag{6}$$

Where ρ g cm^{-3} is the water density. The difficulty is in filling a piece of separator exactly, i.e., no surplus and no deficiency. This paper explains how the technique may be checked and a correction made for inexact filling.

Tortuosity is usually determined from a steady state measurement using a predetermined value of porosity. Separator resistance, R is often used. Thus

$$R = \theta^2 l/\kappa VA \tag{7}$$

Again, the measurement of thickness, l, is an often unsuspected difficulty in eqn. (7).

An alternative procedure [2], not previously tried to the authors' knowledge, is measurement of diffusion ingress into a water-filled separator. At short times the separator may be regarded as semi-infinite, but with diffusion occurring across two surfaces. The equation, with appropriate modification for porosity and tortuosity, is

$$M_t = \frac{4Vc}{\theta}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{8}$$

where M_t mol cm^{-2} is the amount of diffusion ingress in t s and c mol cm^{-3} is the bulk concentration at the separator surface.

Recently it was pointed out that the assumption of a single tortuosity for all pores leads to incorrect predictions in transient situations if the separator actually possesses pores with a range of tortuosities [2]. Comparing a full experimental diffusion ingress curve with theoretical predictions, based on a single or a range of tortuosities, was suggested as a way of establishing the true position. In view of the importance of lead—acid batteries in engine starting, a check for single or multiple tortuosity is an important consideration. A full diffusion ingress curve is reported in this paper.

2. Experimental

Separator

Darak Armorib AR 60 (W. R. Grace Ltd.), a specially produced cellulose fibre separator was used. It is impregnated with phenol—formaldehyde resin to protect the cellulose against chemical and electrochemical degradation. The separator is usually supplied with ribs made from poly-(vinyl chloride), but for this study 5 cm × 5 cm plain sheets without ribs were used in order to simplify interpretation of the data.

Thickness

The thickness was measured with an accuracy of ±0.002 mm using a commercially available unit (Sigmeasure 25). The separator was placed on a flat base and 5 flat, circular contact plates (9.53, 3.19, 1.26, 0.76 and 0.10 mm dia.) were used. The contact plate applied only light pressure to the separator although the pressure per unit area increased as its diameter decreased. The main thickness measurements were made systematically on a larger piece of separator (15 cm × 15 cm) by bringing the contact plate down at 1 cm distances in an orthogonal pattern: 196 thickness measurements were made with each diameter of contact plate. For the three largest diameter contact plates, thickness did not change in the 1 - 2 s required to make and note the measurement. With the 0.76 mm contact plate, the reading sometimes decreased by a maximum of 0.004 mm and with the 0.10 mm plate, the reading decreased by a maximum of 0.02 mm in 1 - 2 s. The thickness was assumed to be that of the initial readings.

Geometric volume

The method used was based on eqn. (6). A 5 cm × 5 cm piece of separator was filled with water under vacuum. 'Excess' water was removed by placing the separator on a dry glass slide and immediately removing it. Trials showed that three such treatments for each surface were sufficient

to remove 'excess' liquid or, more precisely, to give reproducible results. The water-filled sample was then weighed in air and also when immersed in water.

Water content

This is, of course, the difference between the water-filled and the dry weights of the separator. Separators were dried at 110 °C for 1 h.

Diffusion ingress

A 5 cm × 5 cm piece of separator was filled with water under vacuum and then immersed in a beaker in a thermostat bath until a temperature of 25 °C was attained. After 'excess' water had been removed with glass slides, as already described, the separator was immersed in an air-stirred solution of 5.12 molar H_2SO_4 at 25 °C for a timed period. 'Excess' acid was then removed with glass slides and the acid ingress determined by titration with 0.1N NaOH. Practice was necessary to accomplish the treatment with glass slides in minimum time. The separator was washed by immersion in water and the process repeated for another immersion period in the acid. A full diffusion ingress curve was obtained using three different pieces of the same separator.

Surface roughness

Roughness was recorded using a Talysurf 4 with data input to a computer, which calculated the bearing ratio curve. Bearing ratio is defined by reference to Fig. 1 as

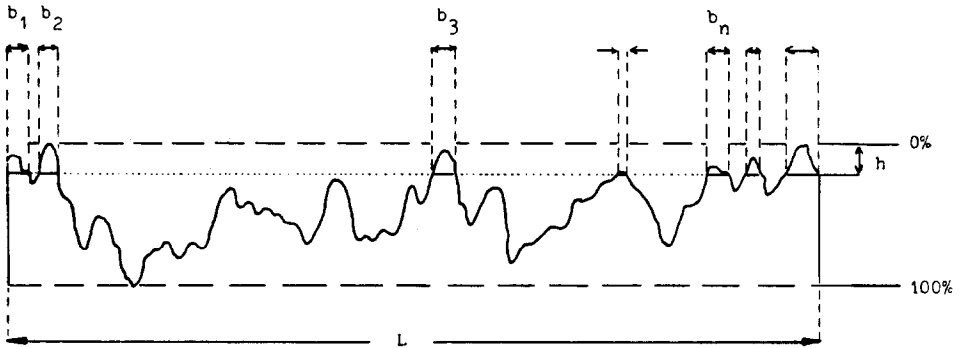$$\text{Bearing ratio} = \frac{b_1 + b_2 + b_3 + \ldots b_n}{L} \times 100 \qquad (9)$$

The bearing ratio curve is the plot of bearing ratio against dimension, h. From this curve, the shaded area shown in Fig. 2 was calculated. The significance of this area was that it allowed an estimate to be made of the surplus liquid collected on the surface of the separator after the glass slide treatment. If B cm^2 is the calculated area for a 0.25 cm-long trace, then the surplus liquid collected in the valleys on both sides of a 5 cm × 5 cm piece of separator is:

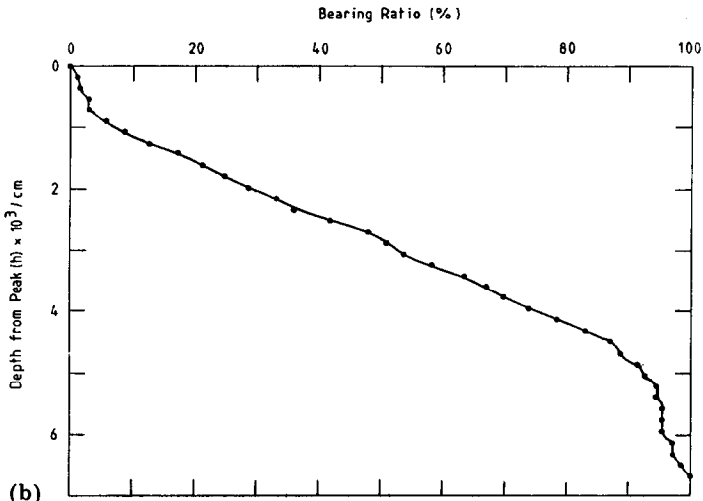$$\text{Surplus liquid (5 cm} \times \text{5 cm)} = 200B \text{ cm}^3 \qquad (10)$$

3. Results and discussion

Direct thickness measurements

Figure 3 shows thickness histograms for different diameters of contact plate. The distribution moves to smaller thicknesses as the diameter of the contact plate decreases. The distributions are skew for the four larger diameters of contact plate but symmetrical for the smallest diameter of contact

(a)

(b)

Fig. 1. (a) Notation of eqn. (9). (b) Median bearing ratio curve.

Fig. 2. Cross-section showing area available for surface liquid.

plate. Plots on normal probability paper, shown in Fig. 4, demonstrate that thicknesses are normally distributed only for the smallest diameter contact plate of 0.1 mm.

The differences in average thickness are substantial, varying from 0.464 mm for the contact plate of 9.525 mm dia. to 0.314 mm for the contact plate of 0.1 mm dia. While the larger thickness is appropriate for deciding the minimum separation of electrode plates in a battery pack, the smaller thickness is probably more applicable when the effect of the separator on ionic mobility is under scrutiny. The normality of the thickness distribu-
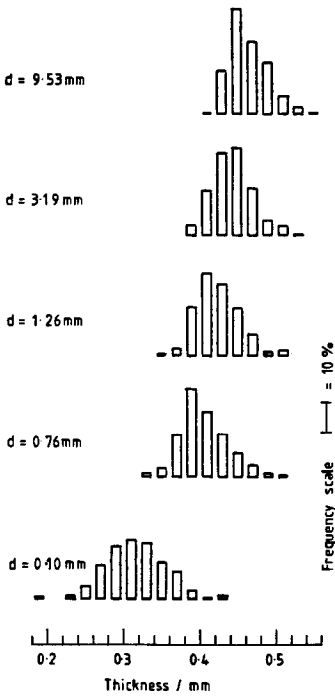
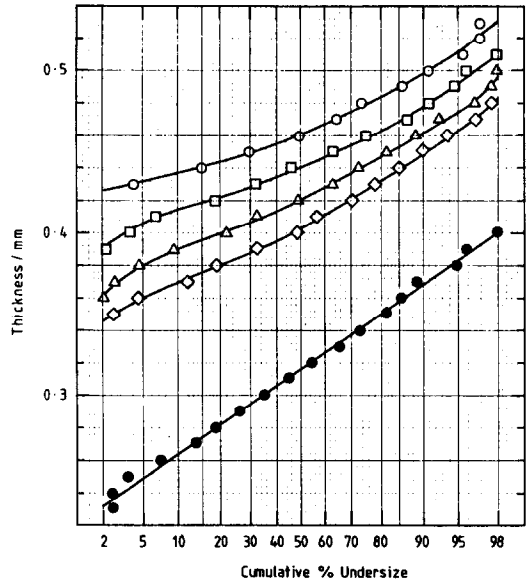Fig. 3. The variation of thickness histograms with contact plate diameter, d.

Fig. 4. Normal probability plots of thickness distributions. Contact plate diameter: ○, 9.53 mm; □, 3.19 mm; △, 1.26 mm; ◇, 0.76 mm; ●, 0.10 mm.

tion is evidence in support of the latter assumption. There is, however, a difficulty. The smallest diameter of contact plate exerted the greatest pressure on the separator material. As noted in the Experimental section, thickness readings changed significantly with time with the smallest diameter of contact plate, which indicates that the separator material was being deformed. While deformation of individual fibres would obviously cause errors, some deformation of the sheet was necessary to bring the bottom surface of the separator into contact with the flat base plate.

These problems arise because of the roughness of the surface. This is inherent in any sheet where the content of separator material is minimised in order to maximise porosity. Figure 5 shows the surface roughness, and Figs. 6 and 7 depict the measurements of thickness with large diameter and small diameter contact plates, respectively.

Figure 8 shows a Talysurf trace, confirming considerable surface roughness.

Diffusion ingress at short times

Figure 9 shows a linear dependence between the amount of diffusion ingress and the square root of time, as required by eqn. (8). The straight lines do not, however, pass though the origin. This is attributed to the
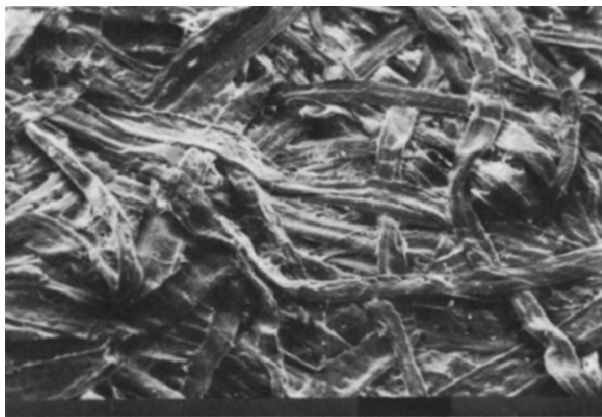
Fig. 5. Scanning electron microscopy photograph of separator surface. Flag, 100 μm.
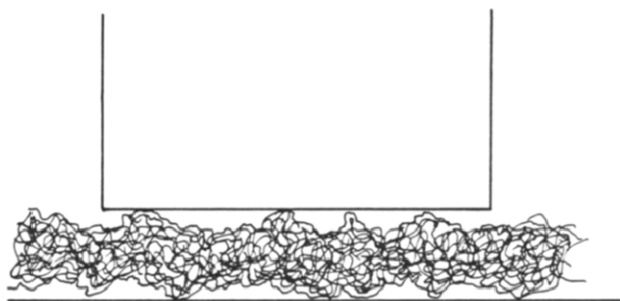

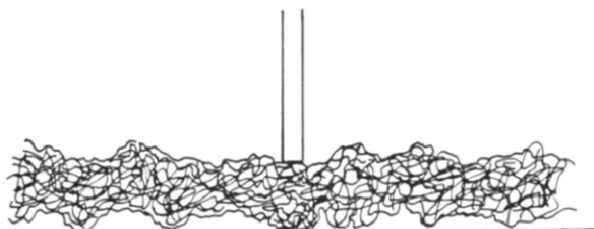Fig. 6. Schematic representation of thickness measurement with a contact plate of large diameter.

Fig. 7. Schematic representation of ideal thickness measurement with a contact plate of small diameter.
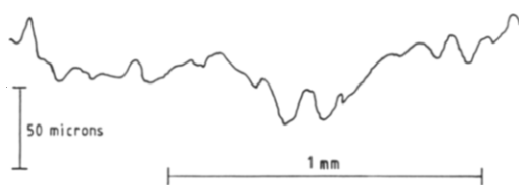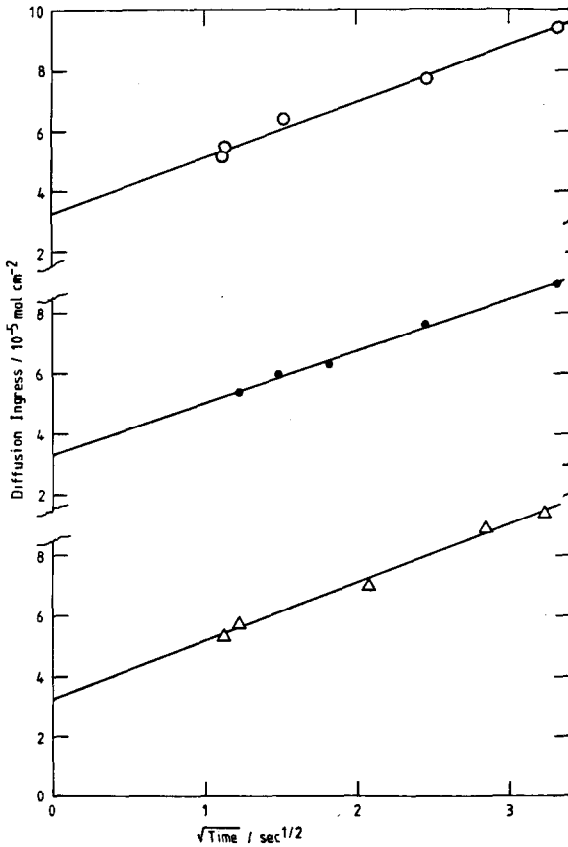

50 microns

1 mm

Fig. 8. Talysurf trace of separator surface.

Fig. 9. Diffusion ingress at short times. O, ●, △ — three pieces of the separator.

inability of the surface treatment with glass slides to remove surface acid held in 'valleys', which was incorrectly recorded as diffusion ingress.

The volume of surface acid was calculated from the magnitude of the intercepts (least mean squares line) and the concentration of the bulk acid. The values obtained for the three pieces of 5 cm × 5 cm separator were 0.160, 0.161, and 0.160 cm^3, which indicates that the glass slide treatment was reproducible in the sense of leaving a consistent volume of liquid on the surface.

Measurement of diffusion ingress at short times is thus a valuable method for checking the consistency of a procedure to remove surface liquid and for estimating and correcting the errors in the procedure.

Surface liquid calculated from the bearing ratio curve

Twenty-one different traces were made with the Talysurf, and from the median bearing ratio curve shown in Fig. 1(b) the value of B in eqn. (10) was found to be 0.765×10^{-3} cm^2 from which, by eqn. (10), the volume contained in the surface topography, *i.e.*, the space available for

surface liquid, was calulated as 0.153 cm³ for a 5 cm × 5 cm piece of separator.

Although the close agreement between this value and the 0.16 cm³ obtained from the diffusion ingress experiments may be a little fortuitous, it is convincing as regards the interpretation of the intercepts in Fig. 9 being due to surface liquid.

Indirect thickness measurement

The geometric volume of the water-filled separator, determined by application of eqn. (6), included surface water. Subtraction of surface water, *i.e.*, 0.16 ml for a 5 cm × 5 cm piece of separator, led to the true geometric volume and thence, by division of the separator area, to an indirect estimate of thickness. The estimates for the three pieces were 0.349, 0.343, and 0.341 mm. The average of 0.344 mm is regarded as a better estimate of thickness than values obtained directly by mensuration.

Porosity

From the true geometric volume and the water content corrected to exclude surface water, the porosities of the three pieces of separator were 0.641, 0.628, and 0.623 (ave. 0.631).

Tortuosity

This was calculated from slopes of the least mean square lines shown in Fig. 9 using eqn. (8), together with values for porosity and the diffusion coefficient of 0.631 and 1.6×10^{-5} cm² s⁻¹ [3], respectively. The value obtained was 1.59.

Full diffusion ingress curve

The theoretical equation [2] governing diffusion ingress at all times for pores of a single tortuosity θ is:

$$\frac{M_t}{M_\infty} = 1 - \sum_{m=0}^{\infty} \frac{8}{(2m+1)^2\pi^2} \exp\left[-\frac{D(2m+1)^2\pi^2 t}{\theta^2 l^2}\right] \tag{11}$$

where M_∞ mol cm⁻² is the amount of diffusion ingress at infinite time into a 1 cm² piece of separator.

The curve in Fig. 10 shows a plot of M_t/M_∞ against $(Dt/\theta^2 l^2)^{1/2}$ calculated from eqn. (11) using $D = 1.6 \times 10^{-5}$ cm² s⁻¹, $l = 0.0344$ cm and $\theta = 1.59$. The experimental data for the three pieces of separator also shown in Fig. 8 are in good agreement with the calculated curve. This is very significant, since such good agreement can only arise if the pores are essentially all of identical tortuosity. This is an important conclusion, as it means for this separator that a tortuosity of 1.59 is valid for both steady state and transient situations. The apparent absence of pores with a distribution of tortuosities is probably the result of considerable interconnection between pores.
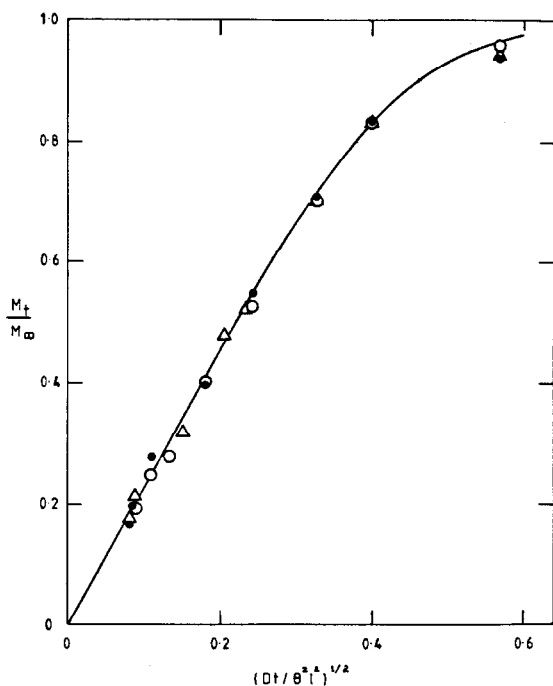
Fig. 10. Full diffusion ingress curve. O, ●, △ — experimental — three pieces of separator; ——, theoretical, $D = 1.6 \times 10^{-5}$ cm^2 s^{-1}; $l = 0.0344$ cm, $\theta = 1.59$.

4. Conclusions

(i) Values for the thickness of separators obtained by direct measurement may be in error and should be treated cautiously.

(ii) Linear extrapolation to zero time of the amount of diffusion ingress plotted against $t^{1/2}$ is a valuable method of checking the consistency of a procedure for removing surplus liquid from a separator and for estimating the amount of surface liquid not removed.

(iii) Measurement of total volume *via* eqn. (6), with a correction for unremoved surface liquid, provides a reliable route to the estimation of thickness and porosity.

(iv) Tortuosity may be readily estimated from diffusion ingress experiments at short times.

(v) All pores in Darak Armorib AR 60 have essentially the same tortuosity, *i.e.*, $\theta = 1.59$.

Acknowledgements

List of symbols

A (cm^2)	Area of separator
b_n	See Fig. 1
c (mole cm^{-3})	Bulk concentration of H_2SO_4 at separator surface
c_+, c_- (g equiv. cm^{-3})	Concentrations of positive and negative ions, respectively.
D (cm^2 s^{-1})	Diffusion coefficient of electrolyte in bulk solution
$\bar{D}$ (cm^2 s^{-1})	Diffusion coefficient of electrolyte in separator
F	The Faraday
h	See Fig. 1
l (cm)	Thickness of separator
L	See Fig. 1
M_t, M_∞ (mole cm^{-2})	Moles of H_2SO_4 entering 1 cm^2 of separator in t s and ∞ s, respectively, through both faces
R (ohms)	Resistance of separator filled with electrolyte
t (s)	Time
u_+, u_- (cm s^{-1})	Mobility of positive and negative ions, respectively, at a potential gradient of 1 V cm^{-1}
V	Fraction of separator volume occupied by electrolyte
v_p	Fraction of separator volume occupied by the inert substance of the separator
W_A (g)	Weight of separator, filled with water, in air
W_W (g)	Weight of separator, filled with water, when suspended in water
κ (ohm^{-1} cm^{-1})	Specific conductivity of electrolyte
$\bar{\kappa}$ (ohm^{-1} cm^{-1})	Specific conductivity of separator
θ	Pore length/separator thickness
ρ (g cm^{-3})	Density of water

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