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PREPARATION OF SILICA AEROGEL FOR CERENKOV COUNTERS

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Preparation of Silica Aerogel for Cerenkov Counters

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Abstract:

Aerogel of silica was produced with an index of refraction of $n = 1.024$ to equip the TASSO Cerenkov detector with 1700 liters of this radiator medium. In the production process, which is described in detail, different parameters were varied to determine their influence on the shape and the optical quality of the aerogel samples. With the present equipment samples with a size of $17 \times 17 \times 2.3\ \mathrm{cm}^3$ were manufactured at a rate of 144 pieces per week. A production efficiency of about 90% was obtained. The index of refraction for all samples around $n = 1.024$ is distributed with $\sigma_n = 1.3 \times 10^{-3}$. They have an optical transmission length of $\Lambda = 2.64$ cm at a wavelength $\lambda = 438$ nm with $\sigma_\Lambda = 0.22$ cm. For samples with $n = 1.017$, Λ is found to be about 30% higher.

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1. Introduction

The application of silica aerogel as radiator[1)] has considerably simplified the construction of Cerenkov counters used in high-energy physics experiments. Indices of refraction which could be obtained only with pressurized gases or gases at cryogenic temperatures are now available with aerogel. It is a light solid medium with sufficient optical transparency. Thus low weight detectors with thin walls may be constructed even in experiments with large counter volumes.

The TASSO detector at PETRA incorporates such Cerenkov counters[2)] which contain a total of about 1700 liters of aerogel with a refractive index of 1.024 covering an area of 11.4 m^2 with a thickness of 13.5 cm. All this material was manufactured at DESY in a laboratory especially equipped for this task.

During the fabrication many parameters were varied to optimize the quality of the gel. Their influence and also the problems which are related to the mass production are summarized in this paper.

2. The Structure of Aerogel of Silica

Aerogel of Silica is a highly porous material normally used as adsorbent or carrier for catalysts[3)]. It consists of small spheres of amorphous silica[4)] bound together to branched strings forming a three-dimensional network whose pores are filled with air. A schematic view of this structure is given in Fig. 1.

The size of the spheres may be computed from the internal surface of the gel which typically amounts to $S = 700\ m^2/g$ [5)]. With a density for the silica[6)] of $\rho_s = 2.2\ g/cm^3$ a diameter of 4 nm is obtained. This small size is also exhibited by a photograph of powdered aerogel taken with an electron microscope (Fig. 2). The diameter of the pores can be computed from the total pore volume V_p by the semiempirical formula[7)] $d_p = 5\ V_p/S$. For samples of our production with $V_p = 8\ cm^3/g$ one obtains $d_p = 60$ nm.

Porous media are of interest in the construction of Cerenkov counters because of their low index of refraction. The index for solid amorphous silica is $n_s = 1.46$. But as the dimensions of the microstructure of aerogel are smaller than the wavelength in the visible region the effective index of the gel is given by an average over the silica and the enclosed air. With the formula of Clausius-Mosotti one obtains

$$n - 1 = \frac{3}{2}\,\frac{\rho}{\rho_s}\,\frac{n_s^2 - 1}{n_s^2 + 2} = 0.19\,\rho \qquad (1)$$

where ρ is the density of the aerogel.

The refractivity has been measured as a function of the aerogel density. Fig. 3 shows that the relationship is linear but with a slope of 0.210 ± 0.002, which is slighty higher than expected from equation (1). The same effect has also been observed in aerogels with higher density[8)] and is probably due to the presence of other molecules chemically bound or adsorbed.

Equation (1) can also be used to derive the ratio of the total pore volume to that of the silica spheres

$$V_p / V_s = (0.41 / (n-1)) - 1 \qquad (2)$$

At $n = 1.05$ this ratio is already 7.4, however it is 60 for an index of $n = 1.007$ which is the smallest index of refraction achieved in our laboratory. These numbers indicate how delicate the structure of aerogel is at low indices of refraction and how sensitively the optical properties depend on the manufacturing process.

The optical quality is mainly determined by the homogeneity of the medium. If structures, clusters of matter as well as pores, occur with diameters greater than about 20% of the wavelength λ, the transmitted light is affected by Rayleigh scattering. With its $1/\lambda^4$ dependence, it dominates at short wavelengths where the Cerenkov spectrum has its highest intensity. The absorption becomes dominant only at wavelengths below 250 nm[9)].

3. Method for the Preparation of Aerogel

The small spheres of silica are formed by the polycondensation of orthosilic acid. During the gellation they are linked together to strings forming the three-dimensional network. Because this acid is not stable as a free substance it has to be generated simultaneously in a parallel reaction.

For the production of aerogels with high pore volumes and good optical properties one has to choose a process whose byproducts can easily be removed. A suitable substance is tetramethoxysilan[1] ($Si(OCH_3)_4$), an ester of orthosilicic acid, which decomposes into the acid and methanol when water is added according to reaction (3). The acid immediately polymerizes to colloidal particles with the release of water (4).

$$Si(OCH_3)_4 + 4H_2O \rightarrow Si(OH)_4 + 4\ CH_3OH \qquad (3)$$

$$n\ Si(OH)_4 \rightarrow (SiO_2)_n + 2n\ H_2O \qquad (4)$$

Both reactions may be accelerated by acid or basic catalysts[10-13]. During the hydrolysis of the ester (3) they supply hydroxyl groups which are added to the silicon atom raising its coordination number temporarily to 5 and repelling the organic radical[10]. In the condensation reaction (4) the catalyst polarizes one hydroxyl group[13] such that up to 2 additional OH groups of other silicic acid molecules may attach to the silicon atom. In the following rearrangement the silicon atoms are then linked by oxygen bonds.

In the polycondensation reaction (4) the molecules grow to colloidal particles with unsaturated hydroxyl groups on their surface (Fig. 4). These groups are normally charged by dissociation or adsorption of ions[14]. Hence the colloids repell each other and come into contact once they have grown to a certain size. Then they are bound by the same siloxan links (Si-O-Si) as inside the particles leading to gellation (Fig. 4). The pores are filled with the alcohol, which is released in the reaction or was initially added (see below).

In this alcogel the bonds between the colloids are almost pointlike leaving the residual surface unchanged with a density of hydroxyl groups[15] of 8 $(nm)^{-2}$. Hence for a typical particle of 4 nm diameter, which contains 700 Si atoms, the condensation reaction (4) has to be modified in order to take these hydroxyl groups into account:

$$700\ Si(OH)_4 \rightarrow [(SiO_2)_{2.5} = OSi(OH_2)]_{200} + 1200\ H_2O \qquad (4a)$$

The OH-groups easily adsorb water molecules which also yield links over longer distances (see Fig. 4). As shown later, these water bonds seem to play an essential role during the gellation and for the stabilization of soft low-density gels.

After the gel is formed condensation of neighbouring unsaturated hydroxyl groups proceeds. In addition, the inverse of reaction (4) - i.e. peptization of the gel - leads to the rupture of siloxan links and, by recondensation with other hydroxyl groups,a rearrangement of the matter takes place. Altogether during this aging the gel structure becomes more rigid but at the same time the size of the particles and of the individual pores increases.

The gel prepared in such a way occupies practically the same volume as the initial mixture. Thus by adding more or less methanol the density and consequently the index of refraction, which later is obtained, is controlled.

To transform the alcogel into an aerogel the liquid inside the pores has to be removed. Methanol and the surplus water are both relatively inert and may be extracted without destroying the gel. But a simple evaporation of the liquid would immediately contract the porous structure because of the surface tension and of the capillary forces. Consequently when stored, the alcogel must always be kept under methanol. To get rid of the liquid the gel is heated in a pressure vessel beyond the critical point of methanol - i.e. 240^0 C and 79.5 bar. Here the methanol is transformed to vapour and may be extracted without harm to the delicate network. When cooled down to room temperature at normal pressure air is sucked in, filling the voids. Some residual methanol and water may be removed afterwards by baking this aerogel at 400^0 C in normal atmosphere for several hours.

4. The Manufacture of Aerogel

As briefly described above, the production of aerogel proceeds in four steps: the chemical preparation of the alcogel, the aging, the extraction of the alcohol, and the baking of the aerogel. In all these processes the texture of the gel may be influenced by various parameters such that the optical and mechanical properties of the gel will change. These procedures will now be described in more detail.

4.1 Installation and Safety Lines

The production of several thousand liters of aerogel implies the handling of large amounts of different chemicals. Thus at DESY a special laboratory was installed for the manufacture of this material.

Both methanol and tetramethoxysilan are inflammable and toxic substances. Methanol is poisonous with an accumulative effect as it is metabolized only slowly. The concentration in air should therefore not exceed 200 ppm[16]. The silan is still more dangerous as its vapor reacts with the cornea[17].

To meet the different safety problems and working requirements the laboratory was subdivided into 3 rooms: one for the preparation and storage of the alcogel, one for the heating processes, and one for final checks of the aerogel samples. The first two rooms are constantly ventilated with an exchange rate of at least 5 times per hour. At certain locations additional ventilation is provided: The mixing is performed under a separate fume hood and the filling of the moulds is done in a box equipped with exhaust fans.

Whenever the silan is handled during the preparation of the gel and when the sol is poured into the moulds, the eyes must be protected by gas-tight glasses. When larger amounts of silan are handled a gas mask is used.

At especially exposed locations sniffers are installed to detect dangerous concentrations of methanol and from time to time the integral methanol content of the air is measured over a period of one day.

4.2 The Preparation of the Gel

To guarantee a constant quality of the gel the initial chemicals must be of high purity (see table 1). The methanol is quoted to be 99% and the water is doubly distilled. Water and methanol are mixed at least one day before use so that the mixture will cool down to room temperature and the water is partly degassed. In recent experiments we found that the extraction of carbondioxide out of the water mixture with sodiumhydroxide improves the transparency of the gel. The transmission length for blue light increased by 10 ± 5%. The tetramethoxysilan is directly procured from the manufacturer with no purity declaration. Comparisons with a "purissimum" quality (≥ 99.5%)[18] revealed no difference. However, when the silan was stored in an opened bottle, the gel became less transparent. Therefore for each batch it is distilled and an equal amount of methanol is added immediately. This mixture turned out to be stable.

To hydrolize and to condensate one mole of the silan two moles of water are needed as shown by equ. (3) and (4). But in practice it turns out that for a homogeneous gel twice as much water is necessary. With lower concentrations the gel becomes milky and investigations by gas adsorption[19] reveal a coarsened structure. As the hydroxyl groups on the surface of the colloids require only 30% more water (4a) the additional amount is required presumably because part of the water is adsorbed on the surface and not available for a homogeneous particle growth.

Water and tetramethoxysilan are not miscible without any additional solvent. A homogenous solution is obtained if at least 1.1 parts of methanol are added to a mixture consisting of 2 parts of silan and 1 part water by volume. For a homogeneous gel half of the methanol suffices, because the chemical reaction uses up water and frees methanol. The amount of methanol determines the concentration of silan in the mixture and thus the density of the final gel. In Table 2 the relative quantities required for two indices of refraction are summarized (see also chapter 4.3).

The chemicals are mixed in a stainless steel pot lined with a polyethylen bag. This is replaced before each new batch is started to reduce the effort of cleaning the utensils. Because both reactions (3) and (4) are exothermic the container is cooled by a waterflushed plate and the liquid is permanently stirred. Just before gelation the sol is poured into the moulds (see appendix) which are then covered by glass plates to suppress the evaporation of methanol. The chemical reactions continue to proceed and heat is still being produced. If a temperature gradient develops in the liquid towards the walls, convection could lead to schlieren which freeze during the gelation. These inhomogeneities contribute to optical scattering and do not occur if the moulds are put onto a plate heated, in our case, to about 30° C.

For one batch we mix a total of 4.25 liters sufficient to produce 6 aerogel samples with a volume of 17 x 17 x 2.3 cm^3 each. The amount of catalyst is chosen such that gelation occurs after 30 minutes with a stirring time of 20 minutes.

4.3 pH Value and Catalysts

Bases and acids are both able to catalyse the hydrolysis of tetramethoxysilan (3) and the condensation of orthosilicic acid (4). Although they act in different ways and with different speeds both lead to amorphous silica. Nevertheless, they produce distinct gel textures since, in solutions with different pH values, the colloidal particles adsorb different amounts of ions. At a low pH value of about 3 the charge of the colloids is low and the particles make contact already when they are of small size. Since also small pore sizes are favoured the gel tends to shrink and becomes more dense[3,5,20]. In solutions with higher pH value the particle repulsion is stronger because of higher surface charges. The particles grow to larger diameters and, in addition, a stable gel with large pores is formed.

This mechanism together with the reaction speed determines the gelling time of the mixture[3]. Its dependence on the pH value of the liquid is plotted in Fig. 5 with the gelling time defined as the period between first mixing and the moment when the content of the mould does not react any more to vibrations. At pH = 2 only a few active ions from the catalyst are present, hence - in spite of the small repulsion - the gelation is slow. At higher pH values (e.g. at 5) the reaction speed overcompensates the increased surface charge and provides for fast gelation. In this pH region hydrolysis is the slower of reactions (3) and (4) and thus determines the gelling time[10]. Therefore, as shown in Fig. 5, the gelation of esters of the silicic acid in methanol takes longer than that of silicates in water which only proceeds via a process similar to (4). Only at high pH values faster gelation of the ester is obtained because of the lower dielectric constant of methanol[21].

The speed of the hydrolysis is proportional to the concentration of OH ions, which for low concentrations is equivalent to the concentration of the catalyst. The same is valid for the gelling speed if the particle repulsion is negligible. For basic catalysts the speed also depends linearly on the concentration of the silan[10]. This is expressed in the following relation which we find for our mixing procedure

$$1/t_g = 6.1 \cdot 10^2 \, (v_S - 0.11) \cdot v_A \; (\mathrm{min}^{-1}) \qquad (5)$$

where t_g is the gelling time, and v_S and v_A the volume concentrations of the silan and the ammonia solution in the mixture, respectively.

This relation is demonstrated in Fig. 6 where the gelling speed is plotted versus $(v_S - 0.11) \cdot v_A$. Equation (5) should only be used as an estimate of the gelling time. The constants of relation (5) depend of course on the temperature, on the concentration of the water, and on the loss of methanol by evaporation during the mixing. They would change if another mixing procedure is used.

It has already been pointed out that high pH values favour the production of large pores. A homogeneous pore size distribution will then arise yielding good optical quality. In Fig. 7 one sees that in the investigated region the transmission coefficient μ for blue light increases linearly with the gelling time which was controlled by the concentration of ammonia. A short gelling time, i.e. a high pH value, is seen to be necessary for good transparency.

The pH value of the mixture and its gelling time may also be altered by higher concentrations of water or by the application of other alcohols or inert solvents. This changes the dielectric constant of the mixture and should therefore influence the particle size. We have observed no further improvements of the transparency when these parameters were varied.

Ammonia is commonly taken as catalyst since it yields stable gels within suitable short reaction times, is easily extracted from the gel and yields aerogels with good optical properties. Other alkaline chemicals such as hexamethyldisilazan (HMDS) (see Table 1) and tris(hydroxymethyl)-aminomethane (Tris) are also suited for catalysis because they decompose at higher temperatures into volatile components. They should be diluted in the methanol-water component before being added to the silan-methanol mixture to guarantee a homogeneous reaction. Only waterfree components, as HMDS, may also be added first to the silan. Their properties were investigated in more detail.

For a silan-water-methanol solution (relative volumes = 2 : 1 : 4.7) the change of the pH value and the temperature was determined during the mixing in our cooled pot (Fig. 8). The pH value, measured with indicator paper[22], drops when silicic acid is formed and the temperature increases rapidly. Ammonia and HMDS behave similarly. In contrast, with Tris the pH value decreases only slightly and the temperature rises slower. Thus cooling is facilitated.

The advantage of HMDS and Tris is their long term stability. Their concentrations remain almost constant unlike dissolved ammonia, which evaporates rapidly if the storage bottles are frequently opened. They should be favoured if the slightly higher transmission coefficient (see Fig. 7) is acceptable.

Another basic catalyst which decomposes easily is ammoniumcarbamate (NH_2COONH_4). But gels prepared with this substance turned out to be milky.

Mass production of aerogel with refractive index n = 1.025 was carried out with HMDS, because it was used during our initial investigations. For practical reasons the mixing was done at room temperature and the gelling time was adjusted to 30 minutes.

4.4 The Aging of the Alcogel

Immediately after gelation the area of contact between the colloidal particles is rather small. Therefore a freshly prepared gel, especially one with low density, is rather soft. Many neighbouring hydroxyl groups may exist, connected only by water bonds. If water and catalyst are still present reaction (4) proceeds in both directions[23] eroding and recondensing matter at the colloids.

Small particles in particular are dissolved and matter settles at the contact regions. Thus in this aging process the bonds between the particles are strengthened. The structure of the gel is coarsened but because of the higher stability it is less affected by the further treatment and the final transparency is better.

In practice, after a gelling time of 2 hours the samples are rigid enough to be covered by a methanol-water mixture. Then the moulds of 2 batches are transferred in a stainless steel rack into a plastic barrel. This barrel contains 22 liters of the same methanol mixture and covers all samples. The alcogel stays in this bath for about 10 days.

The composition of the methanol-water mixture is about the same as within the alcogel, i.e. for samples prepared for n = 1.025 the water content is 6% by volume. For gels with lower density we found that some catalyst (10 cm^3 of NH_3 solution per barrel) should be added.

During the aging period the temperature is kept between 22^o and 25^o C. This guarantees a reasonable reaction speed.

4.5 The Evaporation Cycle

To extract the methanol without harm to the structure the alcogel has to be heated in a pressure vessel beyond the critical temperature. In this process the same reactions occur as during aging but with higher speed due to the elevated temperature. In particular the peptization becomes essential[23].

The erosion of matter is accelerated as the methanol, which expands with increasing temperature, flushes through the pores and takes along peptized colloids. The density of the gel decreases resulting in a lower refractivity and, because the pore size is increased, the optical quality is degraded. On the other hand the samples tend to shrink due to recondensation.

To minimize these processes the extraction should be fast. But the speed is limited because the network of the gel is sensitive to mechanical stresses.

The alcogel samples are transferred to a fresh methanol bath several days before the evaporation cycle to extract part of the water and of the catalyst. This reduces the chemical reactions from the outset. After this treatment the moulds with alcogel from two batches are stacked in the autoclave (described in the appendix) and are fully submerged in methanol. After the vessel is closed it is pressurized with nitrogen to 50 bar to rarefy the oxygen concentration. This is necessary for safety reasons. It also serves to keep the methanol from boiling which would destroy the samples. The temperature is then slowly increased up to 270^0 C within 24 hours, with the pressure kept constant at 120 bar by a relief valve (Fig. 9 and Fig. 10). Then, at constant temperature, the methanol vapor is released in about 6 hours until atmospheric pressure is reached. Afterwards the heating is switched off and the closed vessel cools down to room temperature within about 15 hours. At that time it is opened and air streams into the voids of the gel.

As the methanol expands it flows through the pores of the gel and causes tensions by friction leading to ruptures and reorientations of the network. The forces superpose such that the tensions are highest in the layer most distant to the surface. This is usually the midplane of the sample. In contrast the erosion should affect the outer regions more than the inner ones as the flow increases towards the surface of the sample. Both the coefficient of expansion and the viscosity depend on the temperature. Specifically, at

the critical point the expansion is singular and the viscosity drops by a factor of 5. Thus the direct passage through the critical point should be avoided. For our system the pressure is constant (120 bar) almost over the total heating period. Calculations with this condition and with constant tension inside the gel yield a heating curve as shown in Fig.10. The temperature rises almost linearly up to 215^0 C and then approaches the final value of 270^0 C more slowly.

For samples with $n = 1.025$ such a heating program yields a 13% higher transmission length ($\Lambda = 1/\mu$) than a program in which the temperature rises linearly. A heating period of 24 hours gives best results. If the final temperature is reached within 20 hours the transmission length for blue light decreases by 10%, and for a 48 hour heating it is lowered by 10 - 50%.

The extraction rate of the methanol vapor beyond the critical temperature should be determined by the heating rate near the final temperature. But in practice it turns out that it has to be much faster. For samples with $n = 1.025$ we extract the 50 liters of vapor at 120 bar within 6 hours and for $n = 1.017$ already in 3 hours. This fast extraction seems to be allowed because the esterification of the internal gel surface at high temperature[24] reduces the friction of the methanol.

As expected, an extremely slow extraction degrades the optical quality as well, e.g. if extended to 30 hours for $n = 1.025$ the transmission length is reduced by about 30%.

Despite the slow extraction cycle in our normal procedure an influence of the methanol flow is still observed. Thin samples show a slightly better transparency than thicker ones. For aerogel with a thickness L between 1.5 and 2.5 cm the dependence of the transmission coefficient on L is $d\mu/dL = 0.06 \pm 0.01\ \mathrm{cm}^{-2}$.

Too fast heating and extraction may cause cracks mainly in the horizontal plane. From the optical point of view they are not serious if the light direction is normal to them. The transparency of the samples near these cracks is even higher since there the methanol can escape more easily. Normally they only affect the stability of the pieces and they fill with dust, when the aerogel is cut with a saw.

4.6 Baking of the Aerogel

When the aerogel leaves the autoclave its internal surface is covered by methoxyl groups. The reason is that at high temperature and pressure the hydrolysis (3) is reversed in the methanol atmosphere and the hydroxyl groups are replaced by CH_3O24). Although at most 70% of the OH is exchanged, the CH_3O groups cover the total surface. They shield the remaining hydroxyl groups such that the aerogel becomes hydrophobic. In addition, recondensed methanol is present in the pores. Both contributions also affect the optical properties of the samples. As shown below, the density and thus the index of refraction is increased and the optical transmission is degraded.

The physically as well as the chemically bound methanol may be removed if the pieces are heated in air at a temperature above 200^0 C. The methanol is burned to formaldehyde and formic acid which readily escape25). The internal surface is now covered again by hydroxyl groups which render the gel hydrophilic. At the same time the index of refraction is reduced and the optical transmission is improved. The amount depends on the detailed structure of the gel i.e. on the magnitude of the refractive index n or the transmission coefficient μ, respectively. In our baking procedure we raise the temperature to 400^0 C within 1 hour and keep it constant for 2 more hours. Then the oven is allowed to cool down within several hours. For samples around $n = 1.025$ we obtain the following empirical relations:

$$n_i - n_f = 0.0065 - 0.15\,(n_f - 1) \quad \text{and} \tag{6}$$

$$\mu_i - \mu_f = 0.27 - 0.45\,\mu_f \ \text{cm}^{-1} \tag{7}$$

with the initial and final refractive indices and transmission coefficients. The final transmission coefficient is typically $\mu_f = 0.38\ \text{nm}^{-1}$ measured at $\lambda = 436$ nm, so $\mu_i - \mu_f \approx 0.10\ \text{cm}^{-1}$.

The scattering centers in the final baked aerogel are mainly the larger pores. They contribute to μ_f. Initially these pores are lined with methanol. Their diameters are smaller and scatter less light. This is represented by the second term in relation (7). Larger clusters are formed when smaller pores are filled with liquid. They dominate the total effect and give rise to the constant term in relation (7).

When the aerogel is heated to only 150^0 C for 3 hours it stays hydrophobic and its refractivity decreases only slightly. The transmission becomes worse as μ increases by 5%. The above values are, however, reached when these samples are heated again to 400^0 C.

After the baking the aerogel is more sensitive to moisture in the air. For samples stored in cardboard boxes under normal room conditions a slow decrease in the transmission length (asymptotically to 75 - 90% of the initial value with a mean decay time of 0.5 ± 0.4 month) was observed. At the same time the refractivity increased by 5 - 10%. When exposed to humid air these changes are much faster. But with the baking repeated the former values are again obtained.

If the aerogel is baked twice within a short period at 400^0 C for 3 hours, no further improvement is observed, but the index of refraction increases again, probably due to a slight shrinkage of the gel.

4.7 Volume Changes

The final index of refraction of the aerogel is directly calculable from the densities and amounts of the initial liquids under the assumption that the total volume stays constant. But during production the volume may shrink or expand for various reasons. The index of refraction can be reproduced only if these changes are prevented or occur in a well controlled manner.

When the methanol and water are mixed, the volume of the mixture is smaller than that of the sum of the individual liquids by at most 2%. More serious is the evaporation of the liquid during the mixing. It depends strongly on specific conditions, e.g. the ventilation, the stirring and the temperature. In our case a loss in volume of 10% is observed.

If methanol evaporates after the gelation of the sol, the surface tension compresses the gel to higher density. This can be avoided if during the gelling process the surrounding atmosphere is saturated by methanol or if the sample is covered by methanol later on. On the other hand, this effect may be utilized for the production of gels with higher density than those allowed by the mixing limit. With a slow evaporation rate over several weeks at room temperature samples with an index of refraction up to $n = 1.15$ have been obtained 26). For the same reason the alcogel shrinks in the autoclave if the extraction of the methanol has started before the critical temperature is reached. The samples shrink within a short period keeping their shape. To avoid this effect our autoclaves are heated up to 270^0 C. This is safely beyond the critical point even if some temperature gradient and systematic uncertainties in the temperature measurement are taken into account.

The alcogel is stabilized by the mutual influence of the thermal motion, the attractive forces between the molecular constituents and the ionic pressure 27). Particularly during the aging process and in the pressure vessel the equilibrium may be shifted resulting in a change in the texture of the gel.

The water is very important in this respect. It serves to control the aging speed but, if too much water is used, it contracts the gel structure by water bonds. In contrast, soft alcogels expand if put into pure methanol, e.g. one prepared for $n = 1.01$ doubles its volume. The alcohol extracts some water and consequently removes part of the water bonds. During aging we protect therefore the gels in a methanol bath with a water admixture comparable to that within the alcogel.

During the evaporation cycle in the autoclave the concentrations of water and catalyst should be as low as possible to keep the erosion of matter low. In total the gel tends to shrink during this treatment but soft gels often exhibit signs of a temporary expansion. The shrinkage may be reduced if the expansion of the methanol and the extraction of the vapor is fast enough. The texture of the gel is then stabilized by the internal overpressure and the erosion is limited by lack of time.

A typical value for the lateral shrinkage of our 17 x 17 cm^2 samples during the evaporation cycle is 0.6 - 0.7 cm. This has been observed for all refractive indices between 1.016 and 1.030.

5. Quality of the Mass Produced Aerogel

We are able to fill each of our two pressure vessels 3 times a week so that 90 liters of aerogel are produced in that time. About 90% of the samples produced now show no or only few cracks. To control the production procedure and to select aerogel for the Cerenkov counter systems the optical data of each sample have been measured.

The index of refraction is determined at three different positions by measuring the deflection of a He-Ne-laser beam when it traverses one corner. Measurement of 986 samples with similar production conditions yields a mean refractivity $\langle n-1 \rangle = 25.4 \times 10^{-3}$ distributed with $\sigma_n = 1.3 \times 10^{-3}$. The variation of n-1 within a sample is less than 5% as shown in Fig. 11. In this special case the index of refraction was determined by the lateral shift of an inclined laser beam traversing 2.3 cm of aerogel between two parallel surfaces of the sample.

The apparatus for the determination of the transmittance is sketched in Fig. 12. Light from a halogen filament lamp is filtered at 438 nm and conducted through three light guides to the bottom of an aerogel sample. Three photomultipliers connected to additional light fibres detect the transmitted light at the top. As the sample is pulled through the light beams the intensity is recorded by a plotter. The same group of 986 pieces yields a mean transmission length $\langle \Lambda \rangle = 2.64$ cm distributed with $\sigma_\Lambda = 0.22$ cm. As we have seen in Fig. 8 one could improve the production to obtain transmission lengths of $\Lambda = 4$ cm by faster gelation.

Recently we have started the production of aerogel with a lower index of refraction n = 1.017. The samples show a transmission length which is about 30% higher than for n = 1.024.

A view of a bloc of 6 aerogel samples with n = 1.024 is shown in Fig. 13. When looking diagonally through the stack the writing under the aerogel can still be recognized.

The aerogel samples may easily be cut by a diamond saw to any desired shape$^{2,28)}$. With a disc of 150 mm diameter equipped with grains of size D 356 and a revolution frequency of 2780/min we obtain a very plane surface, which however is coarse like ground glass and scatters light.

6. Appendix

6.1 The Pressure Vessel System

To obtain an aerogel with perfect optical properties the extraction of the methanol in the pressure vessel has to occur in a well controlled way. Two systems are operating at DESY. One of these is drawn schematically in Fig. 14.

The vessels must be able to withstand temperatures up to the critical temperature of 240^{0} C of methanol and the corresponding pressure of 79 bar including some safety margin (see Table 3). Because methanol and water are highly reactive at high temperature stainless steel was chosen for the walls of the containers.

The temperature is adjusted by an analog-program controller in conjunction with a thermocouple which is in contact with the outer surface of the vessel. A mechanical relief valve keeps the pressure constant. The slow expansion is guaranteed by a throttle valve with a needle tip.

6.2 The Moulds

The utmost optical quality of an aerogel sample is obtained if it is cast in

its final shape in a mould with polished surfaces. In the course of the production the alcogel is exposed to different processes which lead to an expansion or a contraction of the substance. Thus the moulds must be conditioned such that the gel can easily be detached from and slide along the walls to avoid the creation of cracks. Glass turned out to be well suited if the edges and corners are rounded with a bending radius of at least 5 mm. However, after repeated use the surface of the moulds lose their necessary smoothness. For test productions cylindrical beakers with volumes of 20 to 500 cm^3 and crystallizing dishes, both made out of glass, up to 3500 cm^3 were successfully used.

Special shapes, e.g. hexagonal gels, are easily made by putting a frame out of an appropriately bent stainless steel sheet into the dishes.

For the mass production quadratic glass dishes of cross section 17 x 17 cm^2 and 3 cm high with a wall thickness of about 3 mm are used. Before each filling the inner surface is covered with a thin film of spray teflon. Treatment with a silicon oil or grease cannot be recommended as this film dissolves in methanol.

Stainless steel dishes with a permanent PTFE surface proved to be disadvantageous as this layer dissolves slowly at high temperature and pressure in the presence of methanol. Moulds out of massive PTFE are well suited as the gel does not stick to the walls. The material expands strongly at high temperatures so that the walls detach from the gel. However, it is very expensive.

At the present stainless steel dishes with inserted walls of 4 mm plastic slices and moulds with removable walls are being tested. After gelation is completed the slices are pulled out and hence the alcogel does not make contact with the walls. With these moulds we succeeded in manufacturing crackfree samples with sharp edges.

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The electron-microscopic picture was taken by Prof. M.Harsdorff and I.Nack from the Institut für Angewandte Physik der Universität Hamburg.

In the beginning of our investigations N.Kuschnerus participated in numerous experiments. Without the continuous and reliable work of U.Balszuweit who manufactured the gels and the diligence of T.Stötzer who was responsible for the optical checks we would not have obtained the present results.

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Table 2 - Mixing Proportions

Index of refraction	Volumes of				Gelling time (min)
	Silane	Water	Methanol	Ammonia* solution x 10^3	
1.025	2	1	4.7	3.3	23
1.017	2	1	8.3	6.7	29

* 1 cm^3 of ammonia solution (see Table 1) is equivalent to about 2.5 cm^3 of HMDS or 3 g of Tris

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Table 1 - Chemicals

Chemical	Formula	Name or Code	Purity %	Producer or distributor
Tetramethoxysilan	$Si(OCH_3)_4$	Dynasil M	(99)	Dynamit Nobel, Troisdorf-Oberlar W.Germany
Methanol	CH_3OH	6008	99	E.Merck, Darmstadt, W.Germany
Ammonia Solution in water ($\geq$ 25% *)		5432	99.5**	-"-
Tris(hydroxymethyl)-aminomethane (or 2-amino-2(hydroxy-methyl)-1.3-propanediol)	$H_2NC(CH_2OH)_3$	8382	99.5**	-"-
Hexamethyldisilazane	$(CH_3)_3Si\ NH\ Si(CH_3)_3$	HMN	98 **	Wacker-Chemie GmbH, Munich, W.Germany

* The actual concentration was not checked

** The contamination due to atmospheric CO_2 is not taken into account.

Table 3 - Autoclave Parameters

Nr.	Effective volume diameter (cm)	Effective volume height (cm)	Material of construction	Closure	max. temp. °C	max. pressure bar	Heating jacket	Manufacturer	Tubes, fittings, valves
1	26	95	stainless steel lining DIN 1.4571	gasket free cone	300	300	electrical infrared 14 kW	E.HAAGE, Mühlheim-Ruhr, W.Germany	Aminco
2	26	95	solid st. steel DIN 1.4571	-"-	350	165	11.6 kW	-"-	-"-

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Figure Captions:

Fig. 1 - Schematic drawing showing the structure of aerogel of silica. The diameter of the spheres is about 4 nm.

Fig. 2 - Powdered aerogel photographed with an electron microscope. The resolution of the instrument is 0.3 nm.

Fig. 3 - Refractivity of aerogel as function of its density ρ. The samples are baked at 400^0 C. One piece was measured before (○) and after (●) baking.

Fig. 4 - Sketch of 2 colloidal particles with hydroxyl groups on the surface arranged as on cristobalite[15)]. One methoxyl group is also present. Both particles are connected by a siloxan link (Si-O-Si) and by a water bond.

Fig. 5 - Gelation time of tetramethoxysilan as a function of the pH value. The mixing parameters were silan : water : alcohol = 2 : 1 : 3.5 (by volume) for $-0.5 \leq pH \leq 4.8$ and 2 : 1 : 5 for $4.8 \leq pH \leq 9.5$. HCl, HCOOH and NH_4OH were used as catalysts. The pH value was determined with indicator paper and is not corrected for the methanol shift. In the region $1 \leq pH \leq 3$ no data could be obtained because of the extremely long gelling time. The full curve is drawn by hand. For comparison the time for forming a hydrogel is also shown[3)] (broken line).

Fig. 6 - Relation between gelling speed $1/t_g$ and the concentrations (by volumes) of silan v_S and ammonia solution v_A (see Table 1) with $C = (v_S - 0.106) \cdot v_A \cdot 10^5$. The line represents Equ. (5).

Fig. 7 - Transmission coefficient μ of aerogel samples fabricated with different gelling times t_g and measured with blue light (λ = 438 nm). The relative volumes were silan : water : methanol = 2 : 1 : 4.7. The straight line represents the points with ammonia as catalyst. The data points for HMDS and Tris have similar errors as for ammonia.

Figure Captions continued:

Fig. 8 - Change of pH value (+) and temperature (·) with time during the mixing (as described in the text). The composition of the mixture was as described in Fig. 7. As catalyst was used: 0.28 cm^3 of a 25% ammonia solution (s. Table 1) or 0.87 cm^3 of HMDS or 0.94 g of Tris per liter. Gelling occured between 35 and 38 minutes in all cases. The pH value is measured as in Fig. 5.

Fig. 9 - V-ϑ-p diagramm for methanol. The extraction cycle in the autoclave follows the broken line.

Fig. 10 - Temperature and pressure inside the autoclave as a function of time. The rise in temperature and the pressure decrease are calculated for constant tension inside the gel.

Fig. 11 - Distribution of the refractivity in an aerogel sample across the 17 x 17 cm^2 surface. The scatter of the points is mostly caused by systematic uncertainties due to the uneven surface.

Fig. 12 - Schematic drawing of the apperatus for the transmittance measurement. Light from lamp L is filtered at 438 nm (F) and arrives through light guides G at the aerogel sample A. Photomultipliers PM detect the transmitted light and send their signals to the plotter P while the sample is moved through the light beams.

Fig. 13 - View of a bloc of 6 aerogel pieces with 17 x 17 cm^2 cross section each and total height of 14 cm.

Fig. 14 - Diagram of the autoclave system. Shown are:
Autoclave A with infrared heater H, security valve SV, and thermocouples TC; gas bottle with inert gas GB, valve V, throttle valve TV, relief valve RV, methanol condenser MC, barrel B, pressure gauge P with electrical readout, plotter PL, analog program for nominal temperature AP, comparator C, and power regulator R.

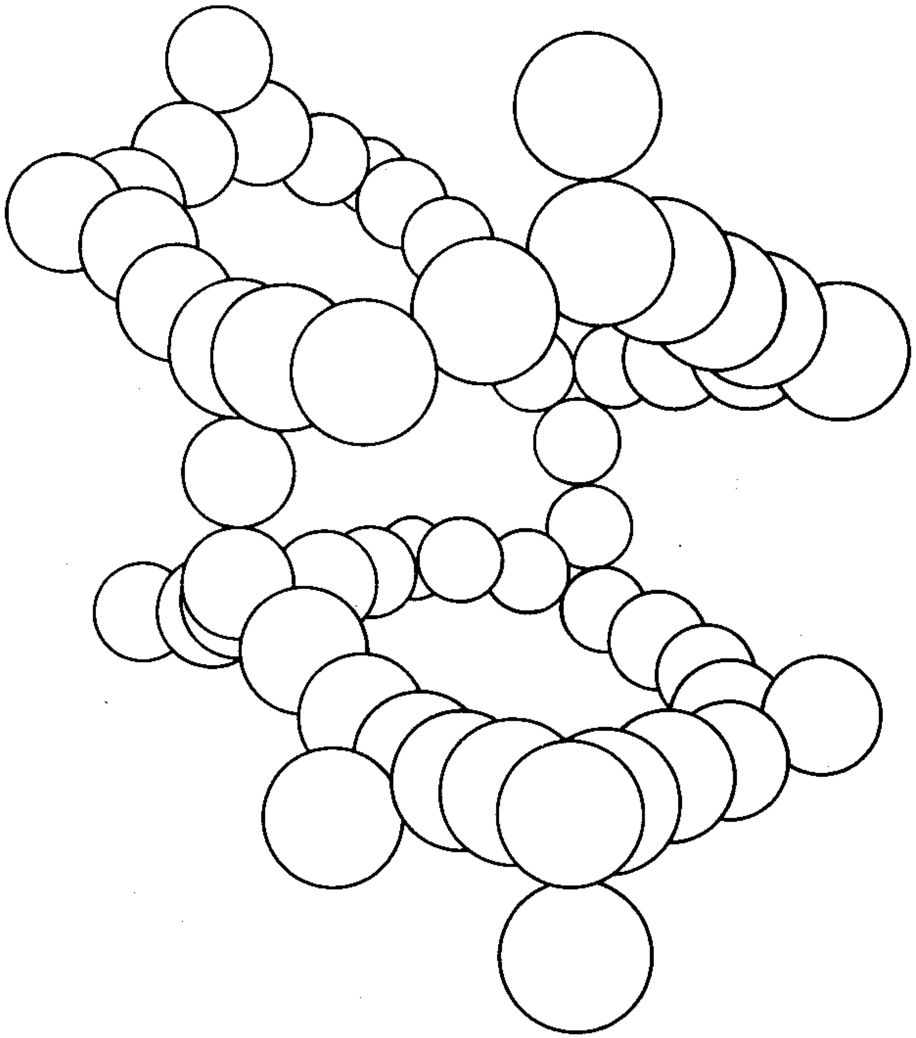

Fig. 1

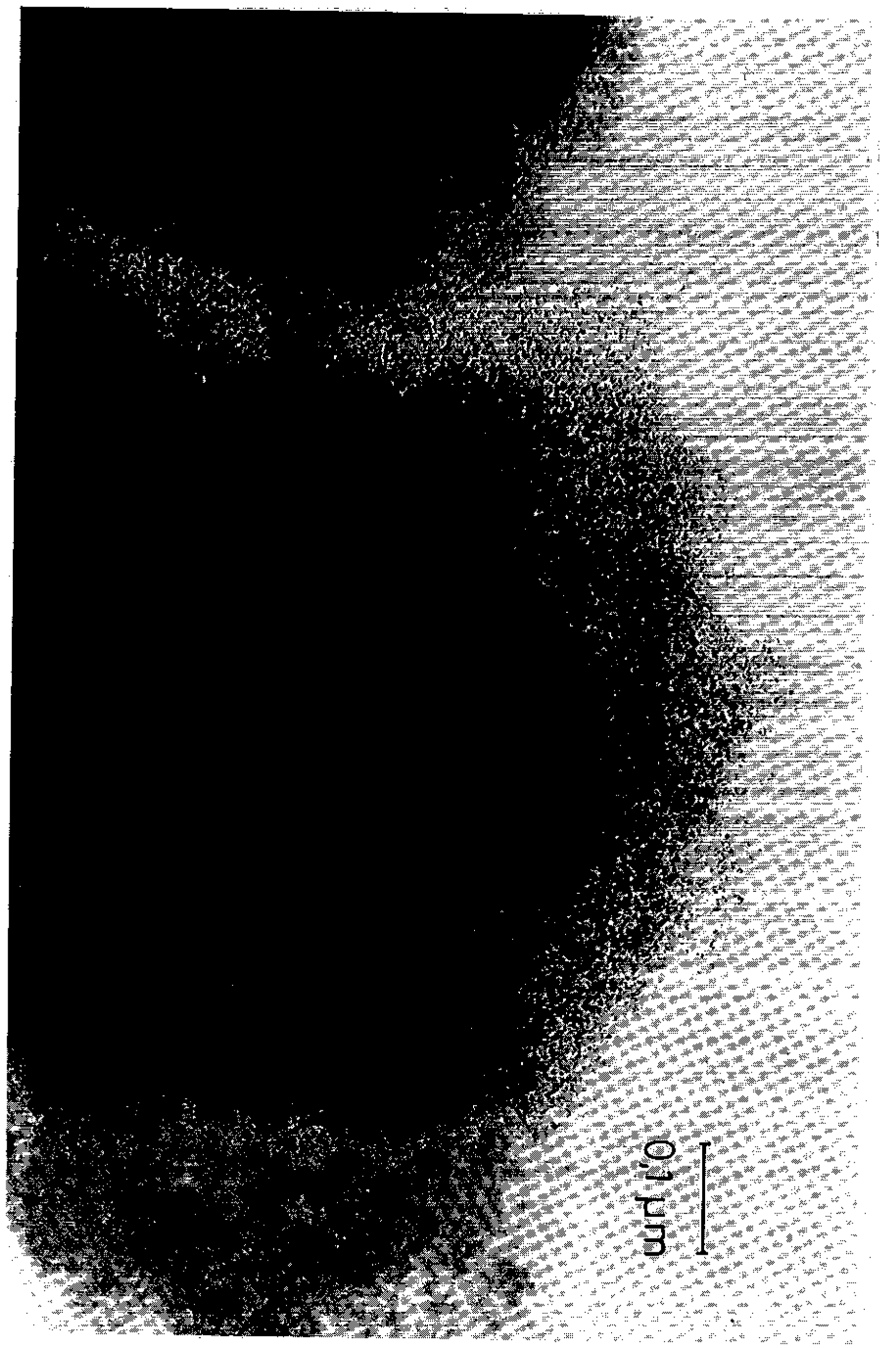

Fig. 2

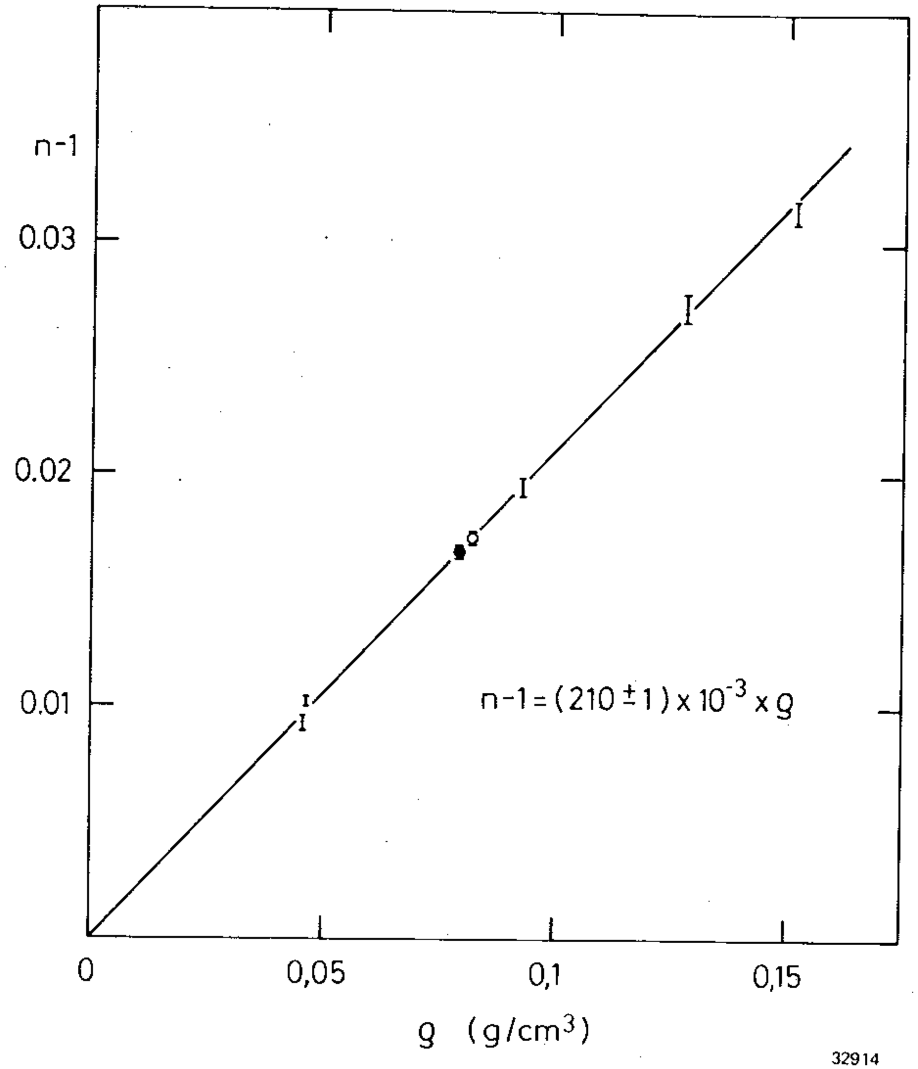

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Fig. 3

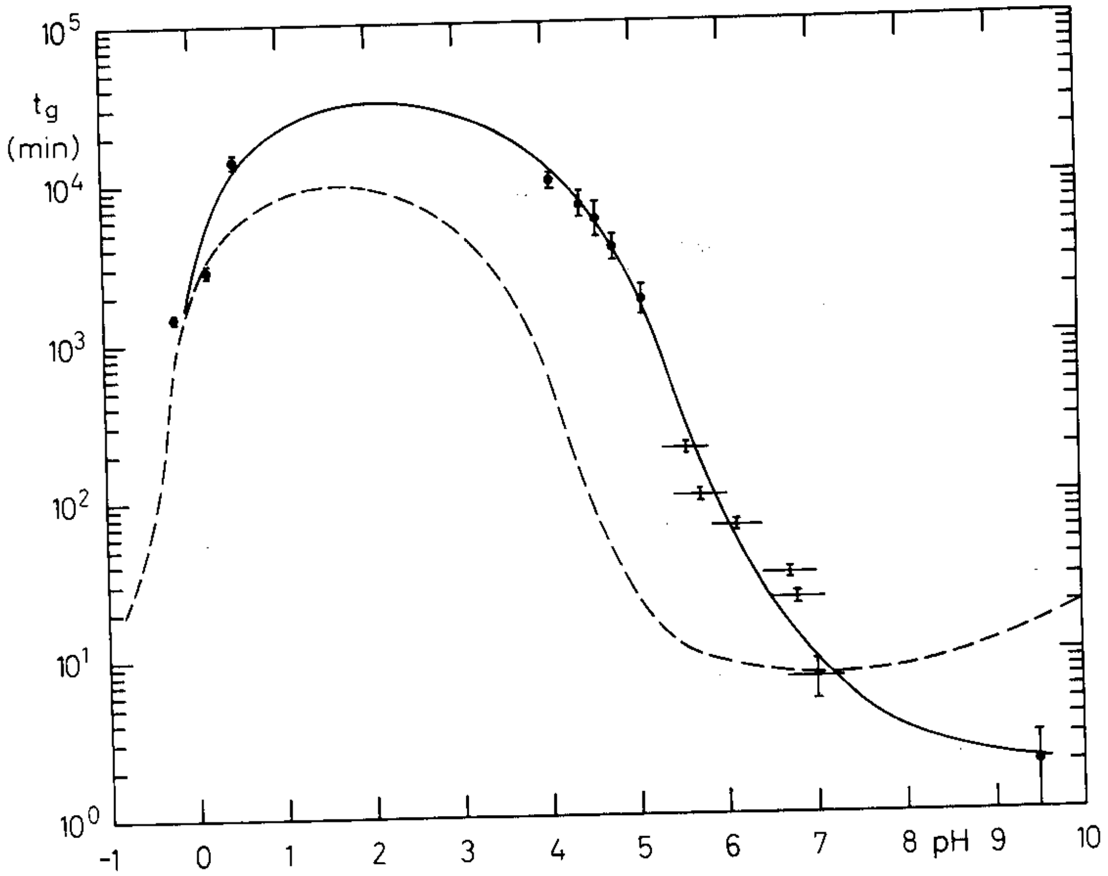
10^5
t_g
(min)
10^4
10^3
10^2
10^1
10^0
-1
0
1
2
3
4
5
6
7
8 pH
9
10
32913

Fig. 5

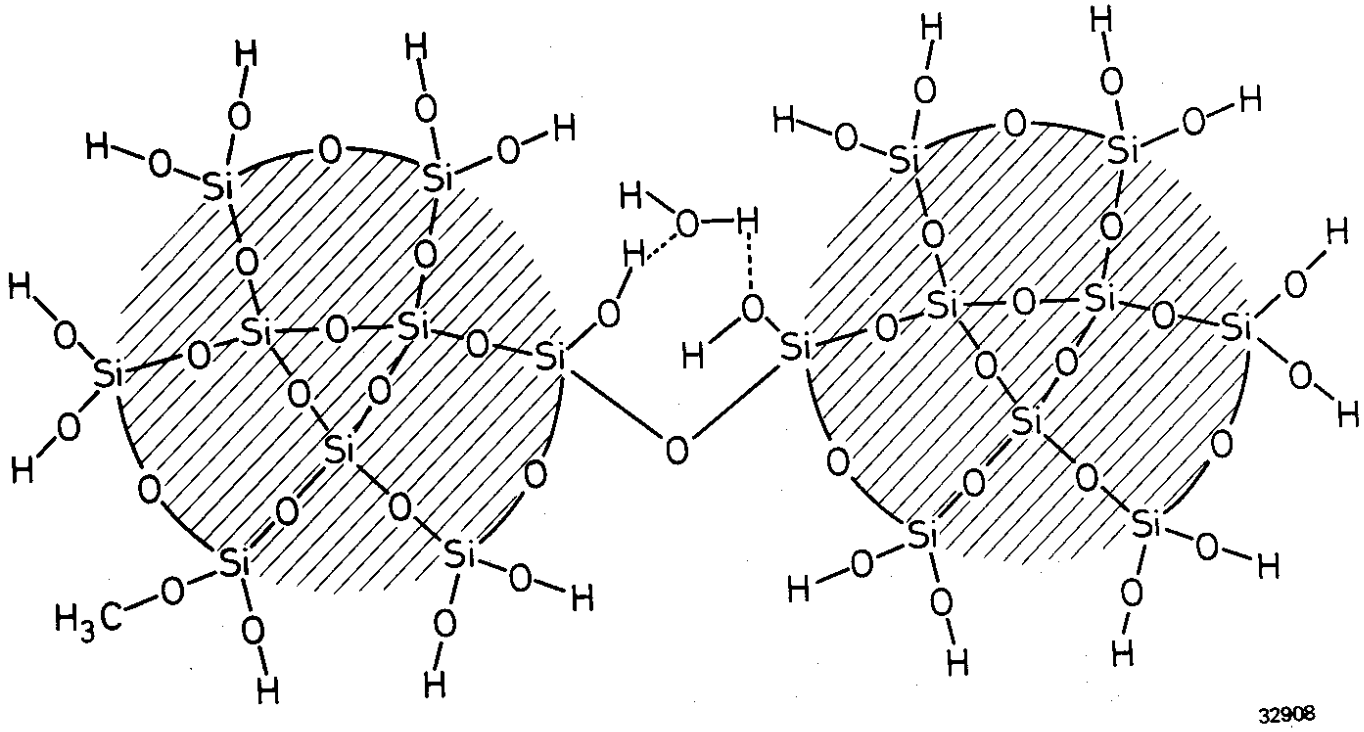
Si
O
H
H_3C
32908

Fig. 4

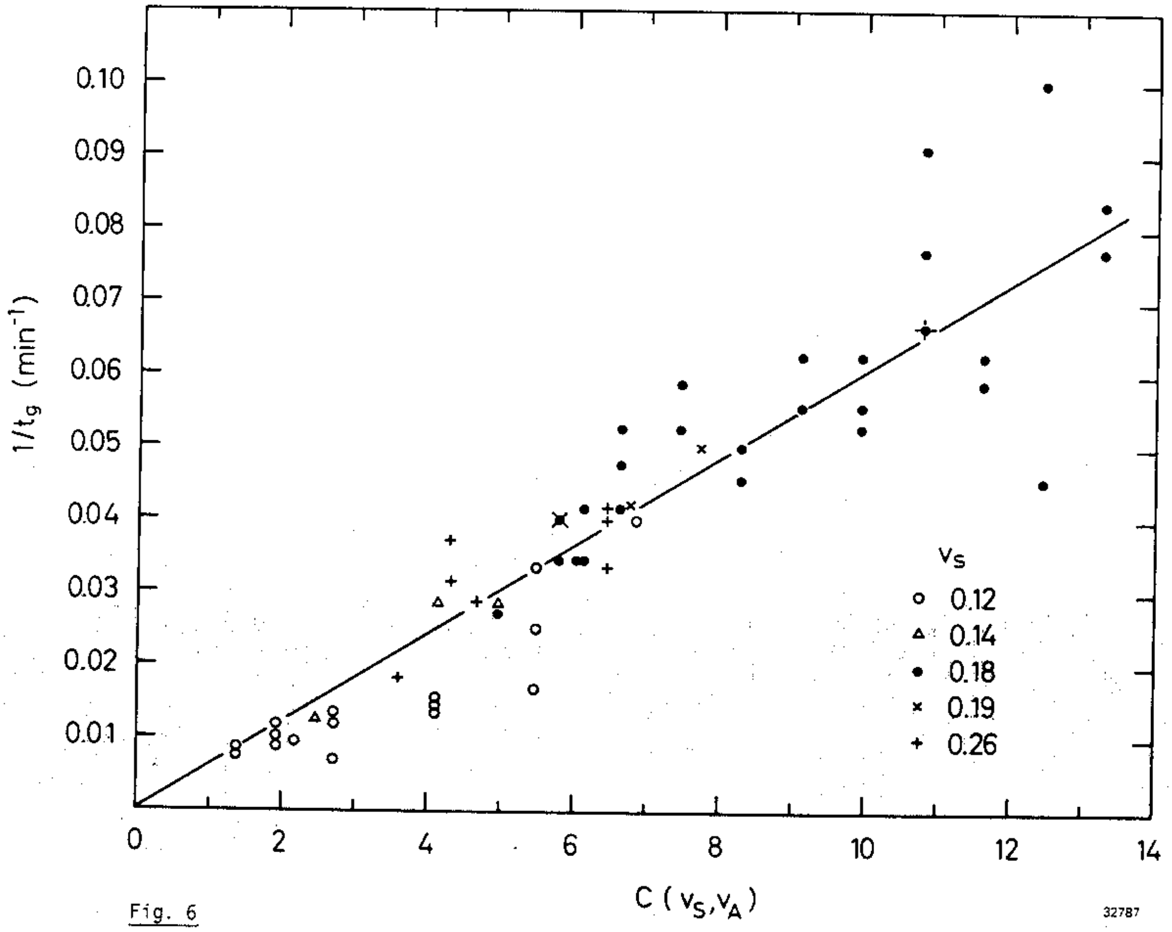
1/t_g (min^{-1})
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
2
4
6
8
10
12
14
C (v_S,v_A)
v_S
○ 0.12
△ 0.14
● 0.18
× 0.19
+ 0.26
32787

Fig. 6

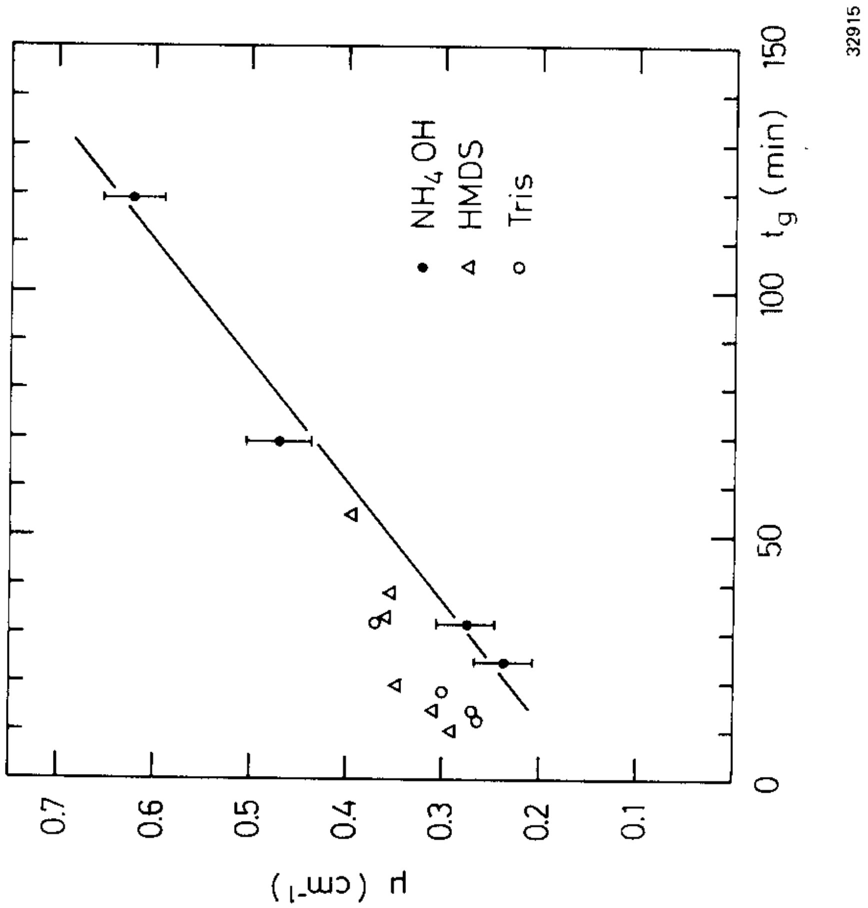
μ (cm^{-1})
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
50
100
150
t_g (min)
● NH_4OH
△ HMDS
○ Tris
32915

Fig. 7

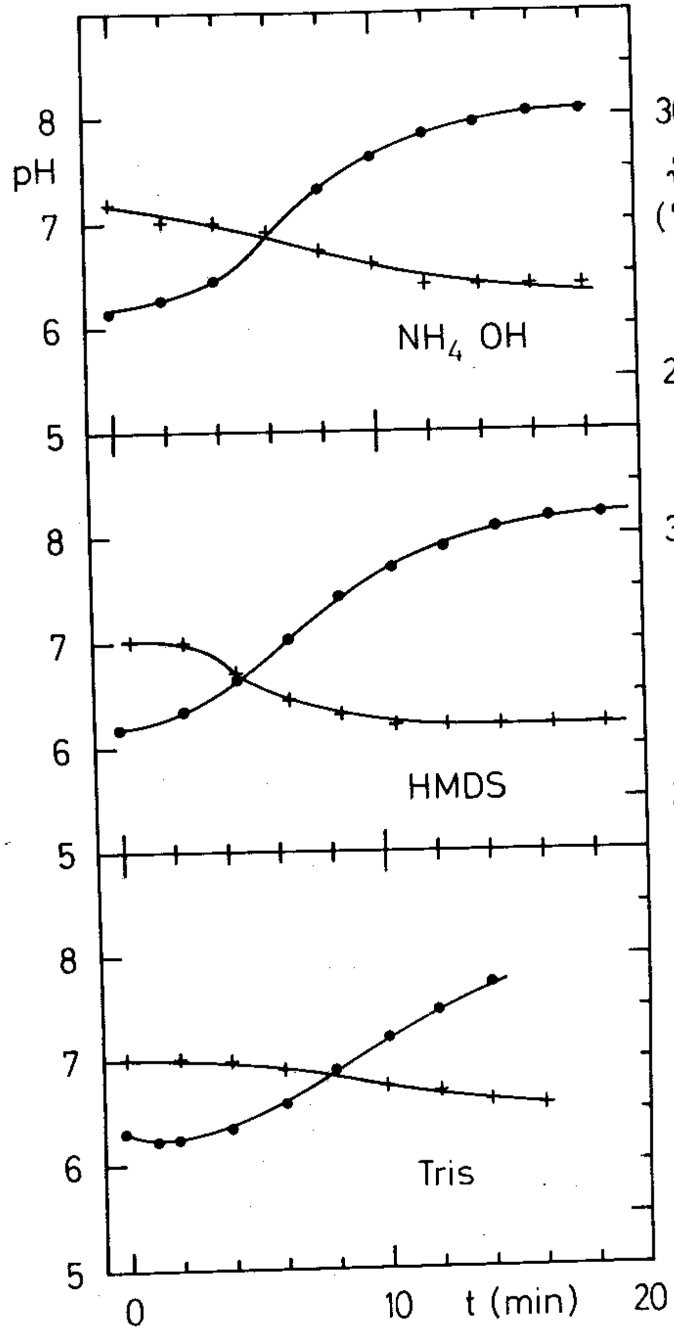

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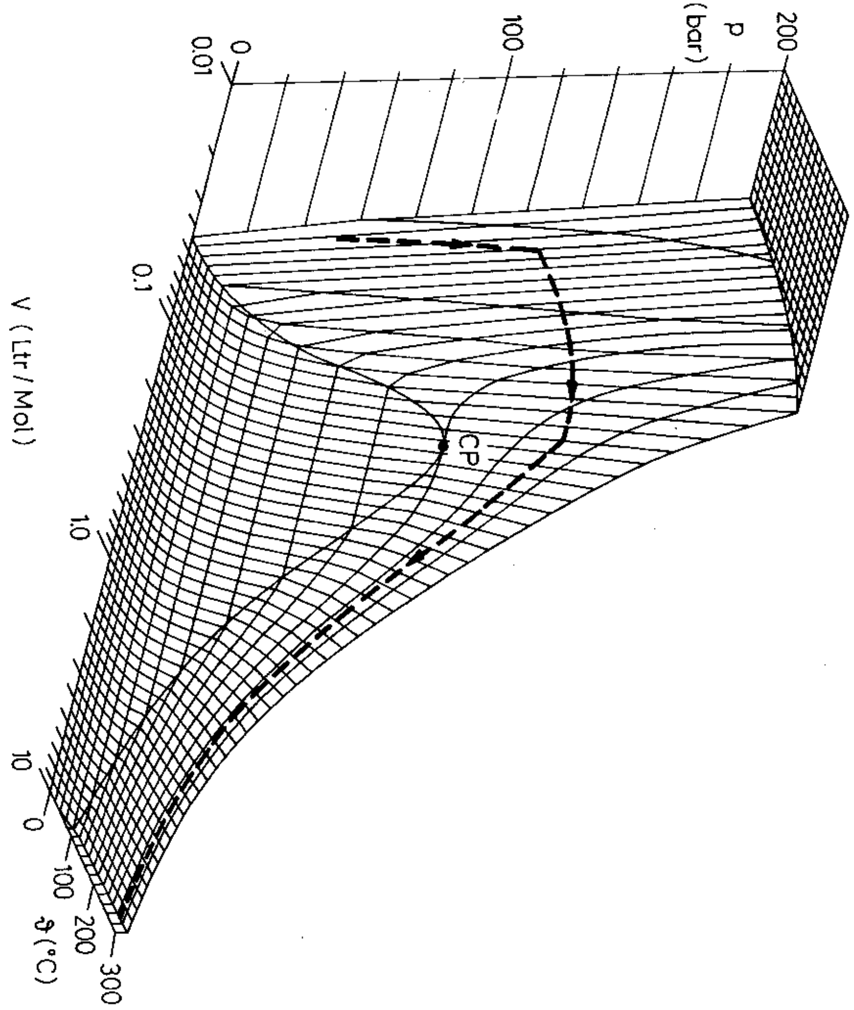
Fig. 8



32917

Fig. 9

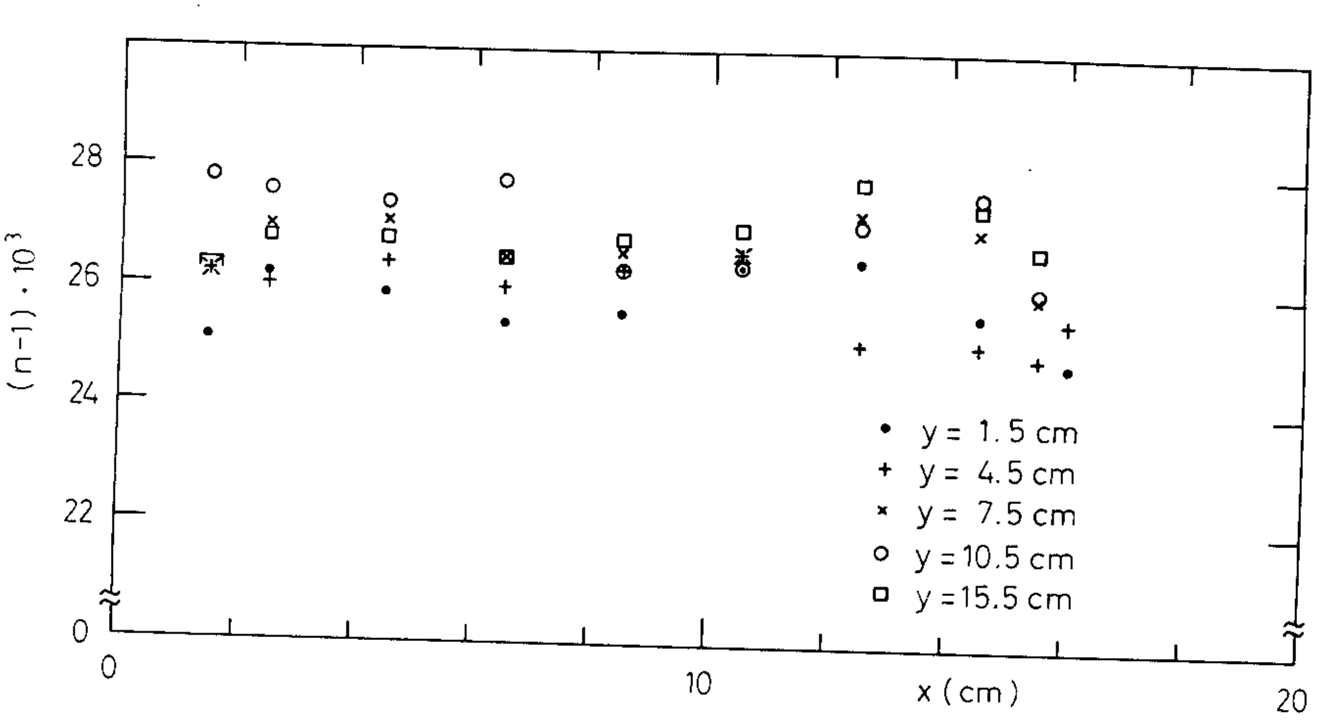


Fig. 11

32910

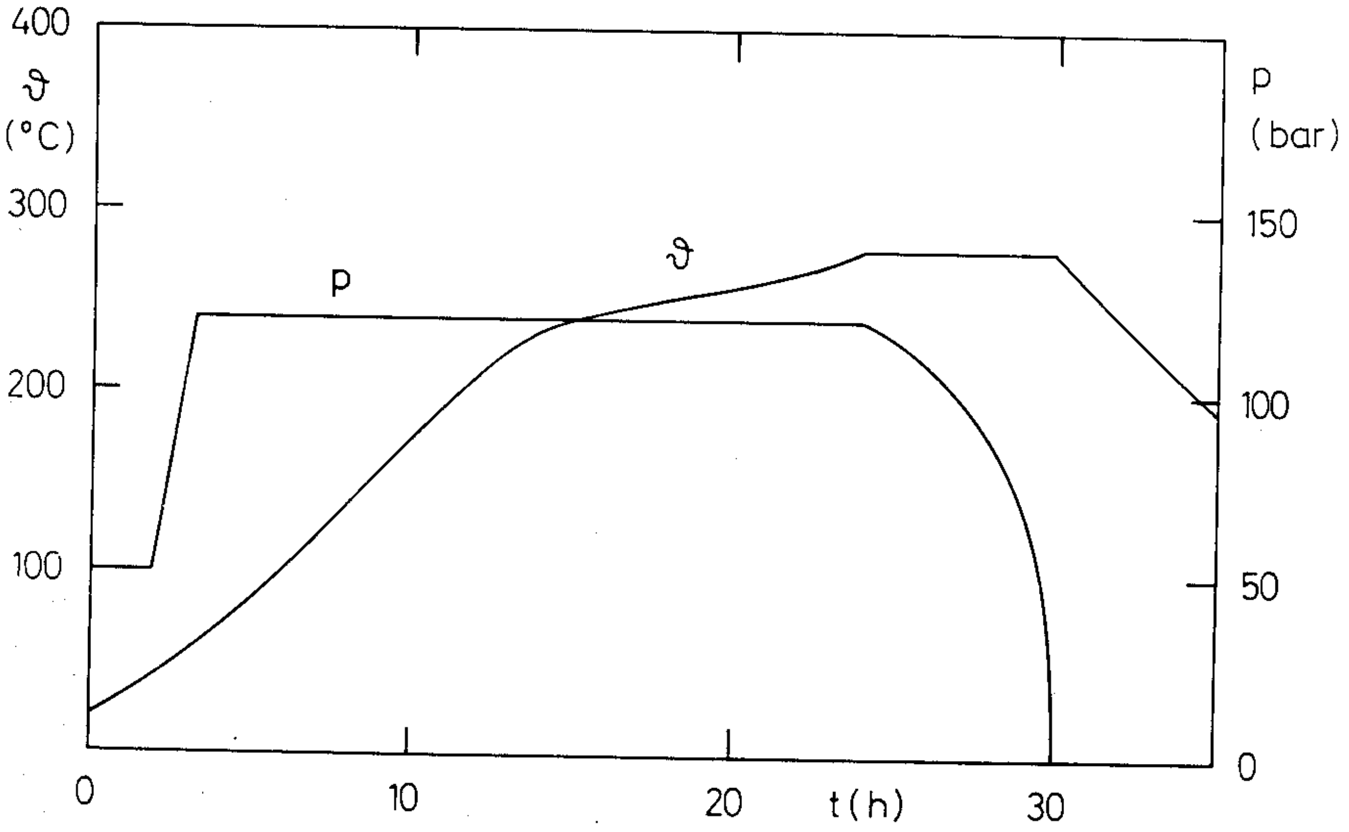


Fig. 10

32909

Fig. 13

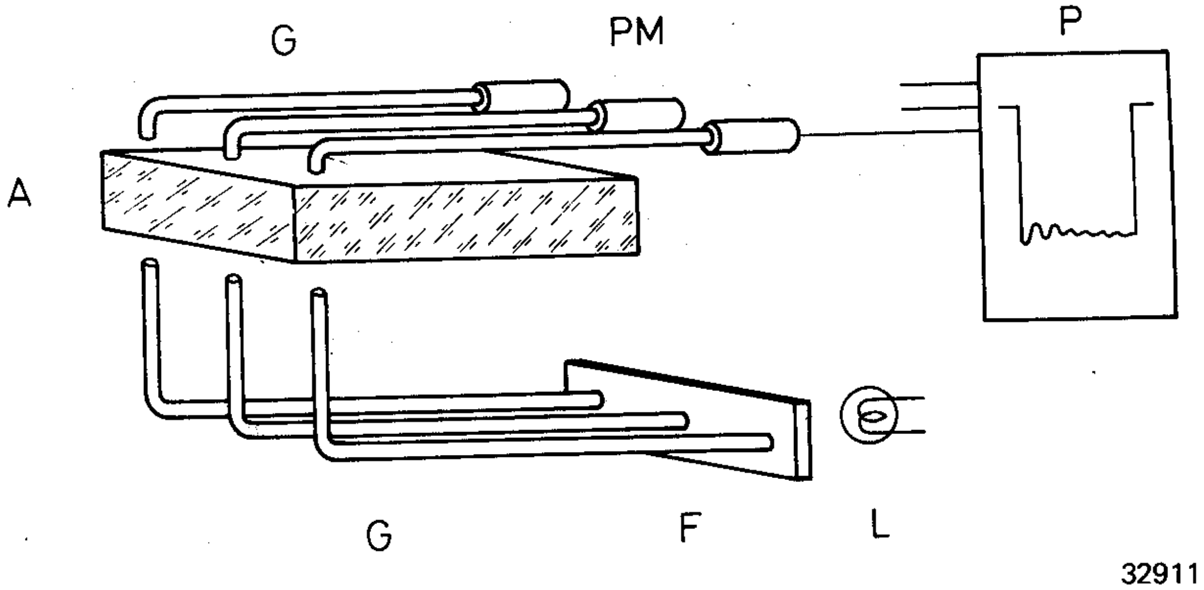


Fig. 12

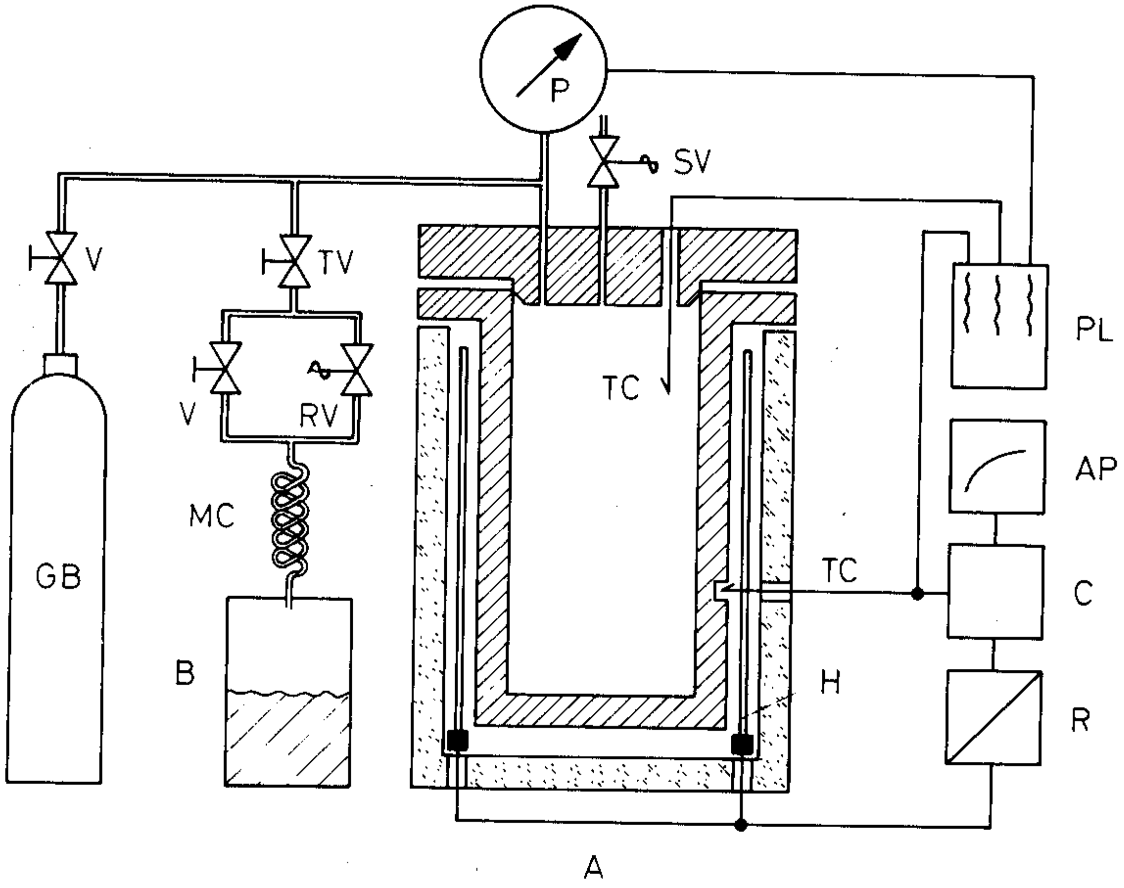


Fig. 14