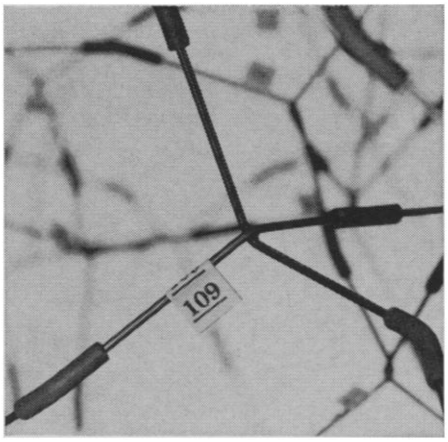

Fig. 1. A wire tetrapod unit as it appears in the random network.

and can be applied rigorously even in constructing a crude mechanical model. The remaining rules involve distances, which can be realized only approximately, and judgments concerning "excessive bending" of bonds which are entirely subjective. Therefore it cannot be said that the tetrapod models are always unique, which would be true of computer-synthesized networks. Computer synthesis in direct analogy to the construction of the tetrapod models is possible in principle, with appropriate mathematical representation of the network's adjustment to local deformation and the criterion of "excessive deformation" in rule 5. It is expected, however, that the most desirable computer synthesis will be a mathematically simpler one not completely analogous to the building of tetrapod models.

Rule 1 may be interpreted as a statement that the condensation process involves a sufficiently low supersaturation and high rate of surface diffusion that each new unit attaches at the site contributing least to surface energy. If the order of preference in rule 1 is reversed, a loose, highly branched structure results which may have its analogue in the fluffy amorphous solids produced by certain condensation processes.

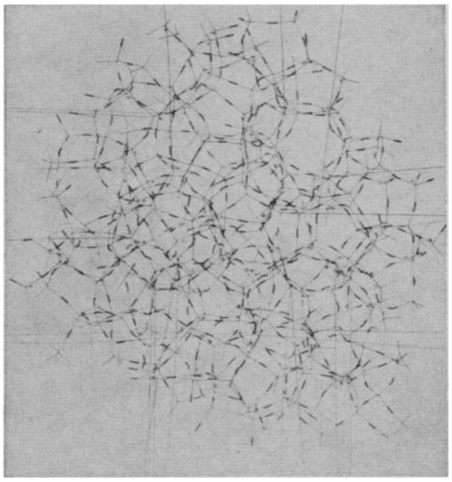

Fig. 2. The random network of 300 tetrapods, with the supporting wires used to hold it rigidly for measurement of coordinates.

Rule 2 may be considered a statement of the fact that the probability of arrival of a new molecule at a given site increases with the length of time the site is available. Rule 6 may be considered a statement that the bond energy and the temperature are high enough for rearrangements to eliminate all interior defects in bonding.

These rules, followed from the beginning, lead to a compact noncrystalline structure (Fig. 2). In the earlier stages it resembles the regular structures proposed by Tilton (*3*) and Pauling (*4*). As the model grows beyond the size of Tilton's "13-unit vitron" (a pentagonal-dodecahedral cage surrounded by a complete layer of similar cages) all further growth is in what may truly be called a random network.

In order to avoid a possible statistical bias a portion of the model containing the regular nucleus could be removed or a nucleus that is not regular could be used at the start. This apparently is the first synthesis of a fully random tetrahedral network, although the tetrahedral network model constructed by Bernal (*5*) may be experimentally indistinguishable. Bernal's model has greater local regularity in that each tetrahedron belongs to at least one five-membered ring having the specific keatite (*6*) configuration.

If a six-membered ring in the chair form is present as an initial nucleus, the same rules lead equally unequivocally to the ideal high-cristobalite structure (*7*) consisting entirely of such rings. If the nucleus is a six-membered ring in the boat form, a cage of the high-tridymite (*8*) structure is produced, but thereafter some five-membered rings develop with inevitable loss of the structural regularity.

The most glaring deficiency of the condensation process under these rules is that sites offering a possibility of forming several bonds at once are given no preference, and therefore the completion of rings and cages is slower than it should be. Correcting this deficiency would, for instance, cause the six-membered ring nucleus in the boat form to produce a perfect tridymite structure. Another improvement in verisimilitude would be to add the tetrapods in groups as well as singly. These changes would increase the complexity of tests or "false starts" during the construction process, at the cost of computational efficiency as is often the case when a Monte Carlo calculation is made more realistic. The construction of satisfactory random network models does not seem to demand such changes at present.

The procedures for efficient, precise determination of the coordinates, and the data on statistical topology and geometry of the random tetrahedral network model containing 300 units, will be published elsewhere.

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Cellulose Acetate Membranes: Electron Microscopy of Structure

Abstract. *Electron photomicrographs of cellulose acetate membranes used in the reverse osmosis process of water desalination reveal a dense surface layer with a porous substructure. The high rate of transmission for water can be correlated with the thickness of the dense layer on the air-dried surface of the membrane.*

Cellulose acetate films have been found effective in the desalination of sea-water brines by the so-called reverse osmosis process (*1*). Recent advances in the technology of film preparation have led to greatly improved water transmission rates (*2*). Preliminary investigation of film structure by optical microscopy has shown that the details of the structure are not apparent at the magnifications used in light microscopy; indeed, the films appear to show no features at × 500 other than knife artifacts introduced during sectioning.

A technique is described here for studying the structure of these films with the electron microscope. The relation of the essential features of the structure to the apparent mechanism for the improved transmission of water is discussed.

The membranes were prepared from a solution of cellulose acetate (39.8 percent acetyl by weight), according to the procedures recommended by Loeb and Sourirajan (*2*). Films were cast on a glass plate with a Gardner film-casting knife at −5°C from a solution of acetone, cellulose acetate (Eastman 398-3), magnesium perchlorate, and water, in amounts of 22.2, 66.7, 10.0, and 1.1 percents by weight, respectively. After 4 minutes, the film was quenched in an ice water bath, and after 1 hour or more it was placed in a water bath at 81°C for 15 minutes. The annealing took place above the glass transition temperature for cellulose acetate, 68.6°C (*3*).

The water content of the finished membrane at 25°C and 100 percent relative humidity was 60 percent by weight. Most of this water is believed to be held in the pores of the film by capillary action. Since the membrane rapidly loses its desalinating property when it is dried, the structure was examined in the wet state.

Spandau and Kurz (*4*) have described the electron microscopic examination of cellulose filters, but in their study it was possible to dehydrate the materials prior to examination. In this report modifications of biological methods (*5*) were used for retaining the three-dimensional pore structure. Small cross sections (1 cm by 100 μ by 20 μ) of a membrane were cut with a conventional microtome equipped with a steel knife. The segments were then placed in an aqueous osmic acid solution (5 percent) for 48 hours. Osmic acid was presumably adsorbed on the internal as well as the external surfaces and was reduced to osmium by the cellulose acetate. The osmium rendered the surfaces more dense to electrons in the electron microscope and thus improved contrast. After the osmic acid fixation, the water within the membrane was replaced with carbon tetrachloride by Soxhlet extraction over a period of several hours. This step did not appear to alter the structure significantly. In a corollary experiment, it was found that membranes treated with carbon tetrachloride behaved in reverse osmosis experiments essentially like the untreated membranes.

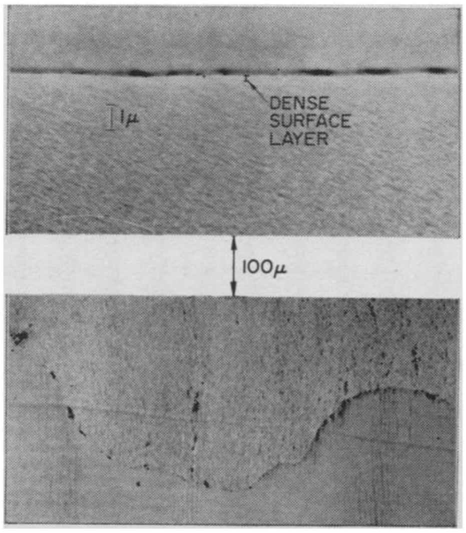

Fig. 1. Composite of two electron photomicrographs of cross sections of modified cellulose acetate membrane.

The carbon tetrachloride was then completely replaced by an epoxy resin by a modification of the Cargille procedure (*6*). The resin solution (1 part epoxy resin araldite 6005, 1 part dodecenyl succinic anhydride hardener, and 1 part *N*-benzyl dimethylamine accelerator) was allowed to diffuse into the membrane segments by placing the segments in successively more concentrated solutions of resin in carbon tetrachloride. Finally, the segments in epoxy solution were placed in gelatine capsules and polymerized at 48°C for 24 hours. Glass knives were used to section the segments into pieces 100 μ by 20 μ by 500 Å on a Reichert thermal-feed ultramicrotome. A tape-collecting trough was attached to the glass knife and filled with distilled water. The thin sections were collected on the water surface from the cutting edge of the knife. After 30 minutes the sections were removed from the water and placed on standard 200-mesh copper electron microscope grids. The thin sections were examined in transmission in the electron microscope.

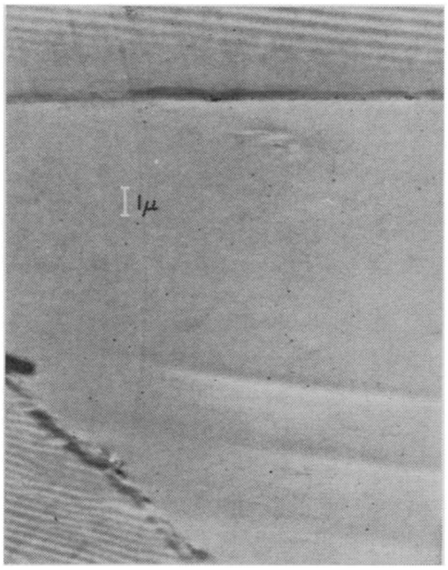

Fig. 2. Electron photomicrograph of a membrane cast from a cellulose acetate-acetone solution and allowed to dry completely in air.

A Hitachi HU-11 electron microscope was used to inspect these membrane sections. Their structural detail, as enhanced by the simple osmic acid stain, did not warrant extremely high-resolution work. Consequently, the instrument was operated as a two-stage system, and the longer focal distance, high-contrast specimen holder was used. An accelerating potential of 50 kv was used to make the contrast maximum. The problem of finding suitable membrane sections was reduced to a minimum by surveying the grids under low magnification with a 100-μ objective aperture. This size provided a usable field of view at magnifications of only 1000 diameters while at the same time there was sufficient contrast to identify the membrane sections. For study purposes, a 50- or 20-μ aperture, used with magnifications of 2000 to 3000 times and with photographic enlargement to 6000 to 9000 diameters, produced better rendition of the microstructure. Focusing of the indistinct image of these sections was enhanced by occasional holes or fine particulate foreign material. The definition of this foreign material showed that a resolution of better than 100 Å could be realized even at these low magnifications. High beam intensities and prolonged exposure times were avoided to minimize damage to the sections. Accordingly, sublimation of the imbedding material was minimized, although in a sufficiently strong section some sublimation could be tolerated and appeared to increase the contrast.

A typical electron micrograph is shown in Fig. 1. It is clear that the membrane consists of a dense surface layer, devoid of structural characteristics, and has a porous, ill-defined substructure. The inability of the osmic acid to permeate the dense surface layer leaves this area transparent to the electron beam. The electron opaque region immediately above the layer results from an accumulation of fixing material. The dense surface layer has a thickness of about 0.25 μ when the total membrane thickness is 100 μ. The remainder of the film appears to be a spongy mass having a pore size on the order of 0.1 μ. The pore structure of the surface cast on the glass is like that of the interior.

For reference, a film cast from a solution of cellulose acetate and acetone and subsequently allowed to dry completely in air is shown in Fig. 2. This film is completely structureless at × 8000 (× 2100; 3.8 enlargement), and it is believed that the thin layer on the surface of the modified film (Fig. 1) is of the same physical constitution as the dense, air-dried film of Fig. 2.

During the several steps in the preparatory procedure it is impossible to remember the identity of each portion of the air-dried surface of the modified film. To effect this identification, a film was pressurized in the reverse osmosis apparatus at 1500 lb/in.^{2} During this step the surface cast toward the glass plate was embossed with the structure of the porous stainless steel backing plate used in the apparatus. This film was subsequently examined in the electron microscope. The dense surface layer was unchanged, while the opposite side contained the embossing, as shown in the lower half of Fig. 1. This montage was prepared from pictures of two nominally identical films and represents the observed structure; it is clear that the dense surface layer is the air-dried surface.

The gross improvement in the rate of water transmission of films prepared as suggested by Loeb and Sourirajan (*2*) is apparently due to the extreme thinness of the dense layer on the air-dried surface. Subsequent studies of the transmission rates of completely dense films 100 μ thick and the modified films show that the rates differ approximately by the inverse ratio of the thickness of this dense layer (that is, 100/0.25), supporting the concept that the permeation is a simple diffusion process and that the variation in permeation rate is a direct result of the effective membrane thickness.

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Sulfate Particulates: Size Distribution in Pittsburgh Air

Abstract. *Sulfate particles with diameters of less than 1.7 microns contribute approximately 40 percent by weight to total sulfate particulate in Pittsburgh air. The irritant nature of these particles and their small size and associated long atmospheric residence time, as well as the short half-life of sulfur dioxide in the atmosphere, suggest that particulate sulfate may be a better indicator of atmospheric pollution than sulfur dioxide.*

In 1955 Hemeon (*1*) suggested that zinc ammonium sulfate was in part responsible for the irritant properties of the fog which occurred during the acute air pollution episode at Donora, Pennsylvania, in 1948. Amdur and Corn (*2*) recently showed that aerosols of zinc ammonium sulfate, zinc sulfate, and ammonium sulfate produce a significant increase in pulmonary flow resistance in guinea pigs exposed to these aerosols for 1 hour. The double salt, which was the most irritant, was studied by generating four aerosol clouds and by characterizing them on a weight basis by their arithmetic-mean particle diameters of 0.29, 0.51, 0.74, and 1.4 μ. We found that the smaller the particles, the greater the irritant action, when the weight of test aerosol per unit volume of inhaled air remained constant. On the basis of the relevance of these findings to the potential effects of urban air pollution on human health, suspended particulate matter in Pittsburgh air was examined for its sulfate content as a function of particle size.

Air samples were collected on the roof of the Graduate School of Public Health during periods of low relative humidity in October and November 1963. A five-stage cascade impactor (*3*) was operated for 1 hour at a flow rate of 18 liters per minute. The collecting slides were coated with a thin film of Fisher Cello-seal; an HA Millipore filter was used for the final collection stage. The washings from slides at each collection stage were analyzed in a spectrophotometer by the quantitative turbidimetric reaction of $BaCl_2$ with sulfate at 420 mμ (*4*); $MgSO_4$ was used for calibration. The analytical procedure was sensitive to 0.5 μg of SO_4^{--} per milliliter in a cell whose pathlength was 40 mm. With the cascade impactor particles were fractionated according to their inertial properties and a range of sizes was collected on each impaction stage. For a given stage, half of the weight collected was associated with particles having diameters less than the mass median diameter. Table 1 shows the weight of sulfate collected and stage mass median diameters calculated for a particulate density of 2.0 g/cm^3 and an assumed reliability of the cascade impactor calibration (*3*). Approximately 35 percent of the sulfate weight is estimated to be associated with particles in the size range found by Amdur and Corn (*2*) to be irritant to guinea pigs—that is, less than 1.4 μ mass median diameter. Atmospheric sulfate concentrations, in the size range of irritant particles, were 0.7 to 7.1 μg/m^3, while concentrations, in the same size range, to which laboratory animals were exposed were 0.25 to 3.6 mg/m^3. However, the arithmetic mean of total suspended particulate concentrations in Pittsburgh from 1957 to 1961 was 0.19 mg/m^3, and a maximum concentration of 0.98 mg/m^3 occurred (*5*). It is not yet known whether these concentrations of mixed particulates, containing less than 5 μg of sulfate per cubic meter, are irritant to guinea pigs or man.

Table 1. Distribution of sulfate in 12 samples collected during October and November 1963. Total sulfate concentrations were 1.9 to 20.4 μg/m^3; relative humidity was 17 to 59 percent.

Cascade impactor stage	Stage mass median diameter (μ)	Total sulfate collected* (%)	Cumulative percentage (wt.) less than stage mass median diameter*
Filter		30.2 ± 8.9	
4th	1.7	24.8 ± 6.4	42.6 ± 9.7
3rd	3.2	18.6 ± 7.9	64.2 ± 10.2
2nd	6.0	14.8 ± 5.9	81.0 ± 7.9
1st		11.6 ± 5.3	94.2 ± 2.7

* Mean ± S.D.