

CHAPTER 2

GEL STRUCTURE AND PROPERTIES

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2.1 GEL PREPARATION AND PROPERTIES:

Eventhough it is true that good crystals can be grown in a variety of gels, the general observation is that silica gels are the best and most versatile growth media. Their preparation, structure and properties, therefore, deserve attention. It may be mentioned that there are no clear-cut demarcation lines between gels, sols, colloidal suspensions, and pastes have been established. A gel is defined as "a two-component system of a semi-solid nature, rich in liquid [1]."

The materials which are generally called gels include not only silica gel [e.g., as usually prepared from sodium metasilicate solution], but also agar (a carbohydrate polymer derived from seaweed), gelatin (a substance closely related to proteins). soft soaps (potassium salts of higher fatty acids), a variety of oleates and stearates, polyvinyl alcohol, and various hydroxides in water. Closest to gels in structure are sols, which are likewise two-component systems, but resemble liquids more than solids.

Gels are formed from suspensions or solutions by the establishment of a three-dimensional system of

cross-linkages between the molecules of one component. The second component permeates this system as a continuous phase. "A gel can be regarded as a loosely interlinked polymer". When the dispersion medium is water, the material is called a "hydrogel". It can be distinguished from the brittle solids which are often obtained by subsequent drying (e.g., silica gel).

The gelling process can be made in a number of ways, sometimes by the cooling of a sol, by chemical reaction, or by the addition of precipitating agents or incompatible solvents. Gelatin is a good example of a substance which is readily soluble in hot water and can be gelled by cooling, provided that the concentration exceeds about 5%. In smaller concentrations, the mixture remains a quasi-liquid, the number of cross-linkages are insufficient to form a gel. In a similar way, non-aqueous gels can be prepared by cooling sols of aluminium stearate, oleate or naphthenate in hydrocarbons. Gels of aluminium and ferric hydroxides, vanadium pentoxide, and bentonite can be made from aqueous suspensions by the addition of suitable salts, e.g., $MgCl_2$, $MgSO_4$, or KCl . Although gelatin gels do not need such additions, their firmness and transparency depend on the pH of the solution before gelling and on the nature of ions present. Preparation of various types of gels has been reported [2,3]. Gels can also be formed by the action

of two reagents concentrated solution, e.g., barium sulfate. from barium thiocyanate and manganese sulfate. This is the type of process which gives rise to silica gels and which, for the present purposes, is the most important. Detailed procedures for the preparation of a whole series of silica-alumina gels of varying pore size have been described by Plank and Drake [4,5]. In these cases, the aluminium salt is dissolved in some acid before mixing with waterglass or sodium silicate. Transparent gels are formed within a few minutes. They have complicated ionic adsorption properties and are ordinarily used as cracking catalysts. When crystals are grown in them, they tend to be contaminated with aluminium [6], which is why they are not generally used for this purpose.

The gelling process itself takes an amount of time which can vary widely from minutes to several days, depending on the nature of the material, its temperature, and history. For silica gel this has been described and discussed by Treadwell and Wieland [6]. During a prolonged period after mixing ("incubation time"). the liquid hydrosol remains outwardly unchange. This is followed by a comparatively rapid and pronounced increase in viscosity and, in due course, by quasi-solidification. Even before this stage is reached, standard viscosity measurements become meaningless because the material is non-Newtonian.

Since gelling is a matter of degree, quoted gelling times are always very approximate. The mechanical properties of fully developed gels can vary widely, depending on the density and on the precise conditions during gelling. For instance, silica gels with a molecular silica-to-water ratio of 1:30 or 1:40 can easily be cut with a knife. At 1:20 the medium is rather stiff, and at 1:10 friable [7]. Still denser silica gels have conoidal fracture surfaces similar to glass. The internal surface area likewise depends on the detailed circumstances during gel preparation [8].

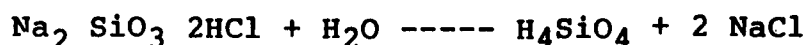
It is often reported that reagents diffuse as rapidly through gels as through water, an observation which dates back to 1862, but it has long since been found that this is true only for electrolytes and very dilute gels. It is certainly not true for large molecules (e.g., organic dyes), nor for colloids. One operative parameter is obviously the size of the diffusing particles, relative to the pore size of the gel. Another is the amount of interaction (if any) between solute and internal gel surfaces. Stonham and Kragh [9] studied the diffusion of KBr through gelatin gels and reported a linear diminution of diffusion coefficient with gel concentration, but no systematic dependence of diffusion on mechanical gel properties. Kurhara and co-workers [10] concluded from their experiments on the diffusion of the sulfate ion in

gelatin gels that the effective diffusion constant is controlled by surface absorption.

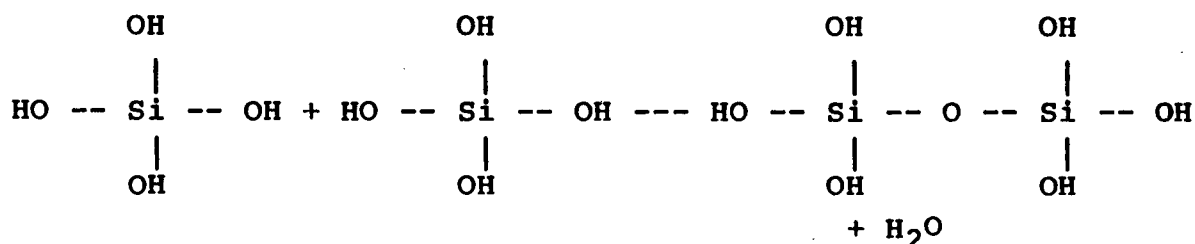
In the course of Experiments on crystal growth in gels, the need to determine reagent concentrations in gels arises frequently, and the adsorptive properties of gels make this a difficult problem. A variety of substances adsorb in silica hydrogel with particular ease. It has been shown [11] for example, that 1 molecule of iron oxide can be adsorbed on every 5 molecules of silica. The chemisorption of alkali ions has been studied by Koopman [12] considering that such gels are generally made from sodium silicate.

2.2 GELLING MECHANISM AND STRUCTURE OF SILICA HYDROGELS:

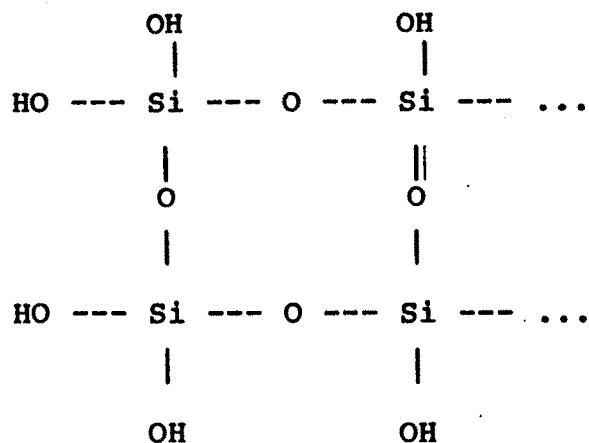
When sodium metasilicate solution (sp. gr. 1.02 to 1.06) mixed with any acid (for example, 1 or 2 N HCl), it may be considered that monosilicic acid is produced, in accordance with the dynamic equilibrium.



and it is generally accepted that monosilicic acid can polymerize with the liberation of water:



This can happen again and again until a three-dimensional network of Si-O links is established, as in silica:



As the polymerization process continues, water accumulates on top of the gel surface, a phenomenon known as syneresis. Much of the water is believed to have its origin in the above condensation process, and some may arise from purely mechanical factors connected with a small amount of gel shrinkage. The time required for gelation is very sensitive to pH. Because gelation is a gradual process, there is no unique definition of gelation time. Hurd and Letteron [13] have described a method of defining gelation time based on mechanical gel properties, and Alexander [14] described a method based on measurement of the reaction rate with molybdic acid. It is still unclear about the gelling mechanism, but it is known that the two types of ions are in fact produced: H_3SiO_4^- , $\text{H}_2\text{SiO}_4^{2-}$, in relative amounts which depend on the hydrogen ion concentration. The latter is favoured by high pH values, is in principle more reactive,

but the higher charge implies a greater degree of mutual repulsion. H_4SiO_4^- is favoured by moderately low pH values and is responsible [5] for the initial formation of long-chain polymerization products. In due course, cross-linkages are formed between these chains, and these chains contribute to the sharp increase in viscosity which is the indication of gelation. At very low pH values, the tendency towards polymerization is diminished, and chain formation is slowed. In the absence of any other reagents, the minimum gelling time is observed at a pH of 8. Gelling time has been found to be strongly dependent on temperature [15]. The formation of cross-linkages can be increased by the partial substitution of Al for Si. Because of the difference in valency cross-links form more easily.

The well-known stability of the silicon-oxygen bonds is responsible for the polymerization process that is largely irreversible. Hurd and Thompson and acetic acid which could be liquefied by shaking. The structure of the Monosilicic acid-water system has been extensively studied [17.18] Light-scattering experiments have been used to study the gelling process [19.20].

It is an interesting fact that when a gel contains bubbles, these are usually lenticular in shape, even though they may begin as spheres in the sol. Their

orientation is often parallel to one another which suggests at least some degree of long-range order. The matter does not seem to have been investigated for silica gels. Hatschek [21] has studied about the formation of bubbles in gelatin gels.

It is now very clear that the basic gel structure affects the crystal growth characteristics, including growth rates, ultimate crystal size and crystal perfection.

Some of the effects of gel parameters on nucleation and growth of KClO_4 crystals will be presented in Chapter 4.

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