

corresponding with either of the other two methods, but approximating to the tension figures. They are definitely higher than the compression figures.

It has been suggested¹ that the differences may be eradicated by making allowance for the changing cross-sectional area of the specimen during test in the case of the extension tests, as this factor was ignored during early experiments and is automatically counteracted in the particular compression apparatus employed. Such correction may be made in tension experiments by calculating the strain on the extended length of the specimen.

Alternatively, where β is not unity, the correction may be made by using the equation :

$$\log \log \frac{l}{l_0} - \beta \log \frac{l}{l_0} = \beta \log s_0 - \log \psi + k \log t,$$

where s_0 is initial value of stress, and l_0 and l are initial and final lengths of the specimen.

Such correction does not, however, entirely account for the anomalies, and it is suggested that the difference is a fundamental one possibly due to the effect of the inter-molecular forces of attraction and repulsion.

The situation with respect to such factors is very complex and will be affected by the physico-chemical as well as the chemical constitution of the material under test. Thus the shape of the molecules, their orientation, their degree of association and their existence in the form of colloidal micelles will all influence the behaviour of the specimen under different types of deformation. General consideration of these inter-molecular forces would lead us to expect a decrease in ψ and k with increasing stress. This decrease is, in fact, found when a single method of test is employed (for example, either extension or compression). That a comparison of results by the two methods does not fall into this scheme may be due to the fact that in calculating ψ and k certain simplifying assumptions have been made which are not true. In particular, it may be that with these particular materials Poisson's ratio is not 0 : 5 as had been supposed.

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March 20.

¹ Broome and Bilmes, *NATURE*, **147**, 176 (1941).

² Scott Blair and Coppen, *Proc. Roy. Soc.*, B, **128**, 109 (1939).

³ Broome and Bilmes, *J. Soc. Chem. Ind.*, **60**, 184 (1941).

⁴ Lethersich, W., private comm. 1942.

Silica and the Liesegang Phenomenon

THE synthesis of a wide range of rhythmic structures, their relationship to naturally occurring forms and the physico-chemical basis common to them have already been studied by one of us (M.C.)¹. The preliminary experiments outlined in the present note extend the application of the Liesegang phenomenon to silica and its hydrates.

Test-tube experiments with aqueous solutions of commercial waterglass (1 : 1 by volume) carefully covered with an excess of concentrated hydrochloric acid at about 17° led to the immediate formation of a fine network structure which soon became a translucent membrane at the interface of the two

liquids. Within 24 hours, 30 white horizontal bands were formed below the membrane. In the course of the next few days the number of bands had greatly increased—occupying more than 80 per cent of the original column of waterglass. The interband spaces increased as the reaction progressed, the 12 bands per cm. below the membrane gradually being reduced to 9 per cm. at the end of the reaction. On standing, the bands, laminated in structure, tended to arrange themselves in groups.

Experiments with more dilute waterglass (3 volumes of water to 1 of waterglass) led to interesting results. The progress of reaction was accelerated and the bands were found to be more closely packed (15 per cm.), aggregating into groups of about four. Above the membrane, in the region originally occupied by hydrochloric acid, a clear jelly-like mass was found (presumably silicic acid gel) equal in volume to about one third that of the waterglass. In some instances, however, the viscous matter exhibited distinct opalescence. Using concentrated waterglass the reaction is slower, the bands are fewer and thicker, being frequently connected by vertical columns of sodium chloride. This is especially the case when hydrogen chloride is the reagent.

In reactions where sulphur dioxide or sulphuric acid had been substituted for hydrochloric acid, certain anomalies were noted, influencing the pattern of depositions. The radial and network structures characterizing the initial stages of membrane- and laminae-formation were superseded by, or rather modified into, concentric ring forms. With concentrated waterglass the interference to diffusion (probably due to the influence of specific colloid-electrolyte complexes) converted the regular pattern of the laminae, as viewed from below, into walnut- and pomegranate-like surfaces. These transitions in the pattern development of the laminae were well demonstrated in beaker and Petri dish experiments, membranes originating in all cases from the periphery of the surface. This dependence of the type of deposition upon the character of the accompanying electrolyte may be of considerable morphological significance.

The fact that the membrane at the interface of the two reacting liquids was at no time distorted by protuberances, particle eruptions or arboreal growth strongly suggests its colloidal character (compare reactions of transitory and permanent colloids as given in earlier publications). Under the experimental conditions used, there was no transition to anhydrous silica, the stratified precipitate remaining in a state of *limited* hydration. The relation of this state to the *unlimited* hydration of silicic acid gel is analogous to that found in the cases of soap curd - soap gel² and hydrocalcite - colloidal calcium carbonate³.

It is intended to use these results as a basis for the synthesis of such minerals as itacolumite (by compression and subsequent dehydration with or without fluxes), opalite, hyalite, etc.

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¹ Copisarow, *J. Chem. Soc.*, **123**, 785 and 796 (1923); **222** (1927). *Koll. Z.*, **44**, 319 (1928); **47**, 60 (1929); **49**, 309 (1929); **54**, 257 (1931). *NATURE*, **129**, 400 (1932). *J. Phys. Chem.*, **36**, 752 (1932). *Science*, **77**, 581 (1933). *Protoplasma*, **30**, 258 (1933).

² Laing and McBain, *J. Chem. Soc.*, **118**, 1506 (1920). Marton, McBain and Vold, *J. Amer. Chem. Soc.*, **63**, 1990 (1941).

³ Copisarow, *J. Chem. Soc.*, **123**, 785 (1923).