

A weighed quantity (0.2 g.) of  $ZnSO_4 \cdot Ti(SO_4)_2$  was boiled with distilled water (350 cc.), the metatitanic acid filtered off and the sp. conductivity in mhos./cm. of the filtrate (made to 100 cc.) was determined by the method of Kohlrausch. This filtrate was again diluted with an equal volume of distilled water and sp. conductivity measured. This operation was repeated thrice. Similar measurements were made with solutions prepared from the calculated amount of zinc sulfate and sulfuric acid. The values thus obtained which are reported in Table I, are very close to each other showing thereby that the hydrolysis takes place according to the expression given before and the substance  $ZnSO_4 \cdot Ti(SO_4)_2$  behaves as a double sulfate.

TABLE I

SPECIFIC CONDUCTIVITY OF HYDROLYZED SOLUTIONS AND SYNTHETIC SOLUTIONS OF SAME CONCENTRATION

Solution	Sp. conductivity, mhos. $\times 10^{-3}$				
$ZnSO_4 \cdot Ti(SO_4)_2$	5.61	3.05	1.76	0.91	0.48
$ZnSO_4 + H_2SO_4$	5.48	2.94	1.67	0.89	0.46

The other compounds of the type  $RSO_4 \cdot Ti(SO_4)_2$  were also examined and showed similar behavior.

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### Elastic Constants of Gelatinous Substances

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The importance of measurement of elastic constants of gels is threefold, *viz.*, (1) it provides a basis for comparison with other substances; (2) it furnishes a criterion for studying the semi-solid nature of gels, and (3) it affords a basis to understand the ultimate mechanical behavior of gels. From the knowledge of variation of these quantities with frequency, temperature and other factors, conclusions may be drawn to elucidate the mechanism of gel formation and the internal structure of the gel.

The method<sup>1</sup> is an adaptation of the ultrasonic technique developed by Pellam and Galt,<sup>2</sup> modified by Teetar<sup>3</sup>; it is based on the theory of Knott.<sup>4</sup> Ultrasonic waves are generated by a suitable pulse transmitter, impinged upon a slab of gel, received by a quartz crystal and detected after proper amplification on a cathode-ray tube. The rotation of the slab in a vertical plane changes the angle of incidence of these waves and in two positions sharp minima in the transmitted intensity are observed due to the total reflection of the two waves set up in the gel. These two waves are due to the resolution of the incident beam into longitudinal and transverse components.

From the two critical angles,  $\theta_c$  and  $\theta_s$ , the velocity of the waves  $V_e$  and  $V_s$  can be computed. A knowledge of these and the density  $\rho$  of the gel gives the elastic constants from the relationships

$$V_e = \frac{V_{water}}{\sin \theta_c}; \quad V_s = \frac{V_{water}}{\sin \theta_s}$$

$$V_e/V_s = k; \quad \sigma = \frac{k^2 - 2}{2(k^2 - 1)}$$

$$V_s = \sqrt{\frac{S}{\rho}}; \quad E = 2(1 + \sigma)S$$

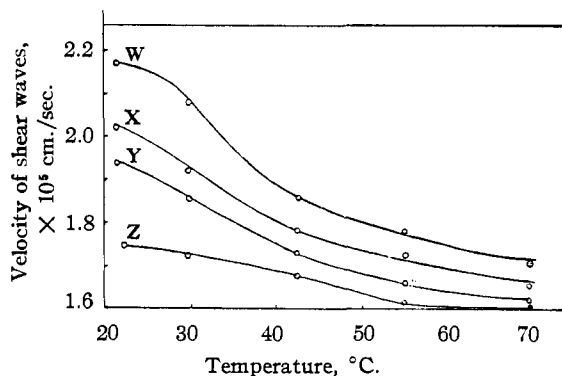


Fig. 1.—Iron silicate gel: velocity-temperature relationships: W, 2.500 ml./s.; X, 2.250 ml./s.; Y, 1.250 ml./s.; Z, 0.625 ml./s.

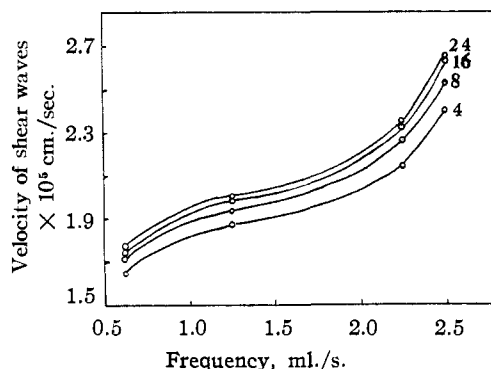


Fig. 2.—Iron silicate gel: velocity-frequency relationship at 30°; 4, 8, 16 and 24 hours.

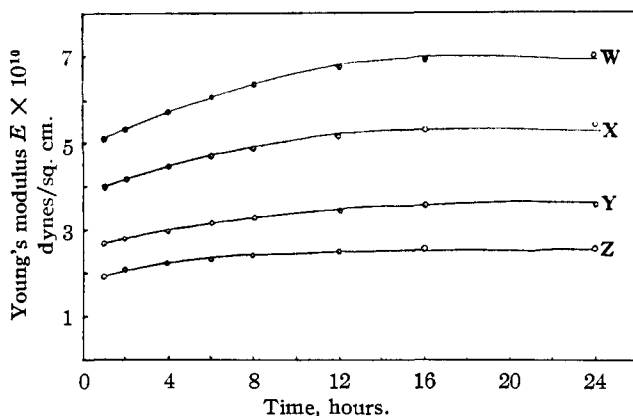


Fig. 3.—Iron silicate gel showing variation of  $E$  with time at 30°: W, 2.500 ml./s.; X, 2.250 ml./s.; Y, 1.250 ml./s.; Z, 0.625 ml./s.

where  $\sigma$ ,  $E$ ,  $S$  are the Poisson ratio, Young modulus and Shear modulus.

The values obtained for the various constants are plotted in Figs. 1-3. The four frequencies used were, 0.625, 1 250, 2 250 and 2.500 Mc./sec.

(1) A. M. Srivastava, *Proc. Nat. Acad. Sci., India*, **18A**, 51 (1949).  
(2) J. R. Pellam and J. K. Galt, *J. Chem. Phys.*, **14**, 608 (1946).  
(3) C. E. Teetar, *J. Acc. Soc. Am.*, **18**, 488 (1946).  
(4) C. G. Knott, *Phil. Mag.*, **48**, 64 (1899).

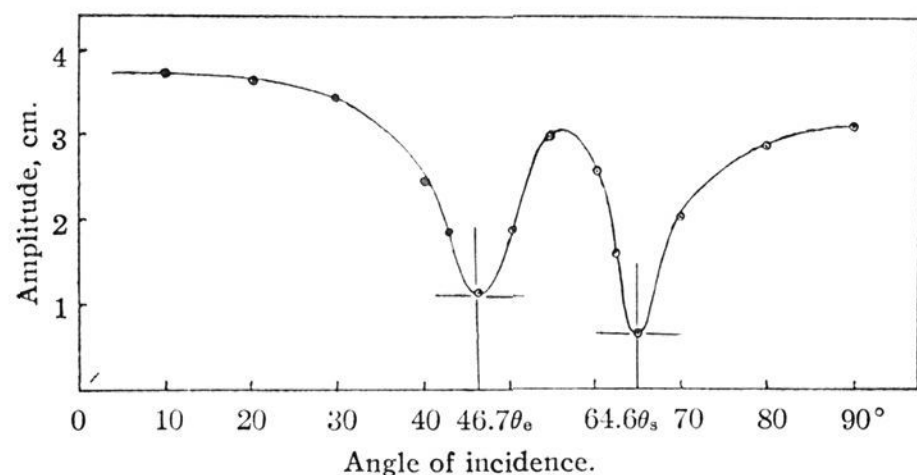


Fig. 4.—Showing the variation of amplitude with angle of incidence:  
 $V_e = 1.55 \times 10^5 / \sin \theta_e$ ;  $V_s = 1.55 \times 10^5 / \sin \theta_s$ .

Density of the iron silicate gel, for which these results are given, was 1.180 at  $23^\circ$ . Figure 4 shows the variation of the amplitude of the transmitted rays; the two dips correspond to the values  $\theta_e$  and  $\theta_s$  in a particular case. Figure 5 is the oscillogram in which A is the instant of start of the ultrasonic pulse and B the amplitude of the transmitted waves.

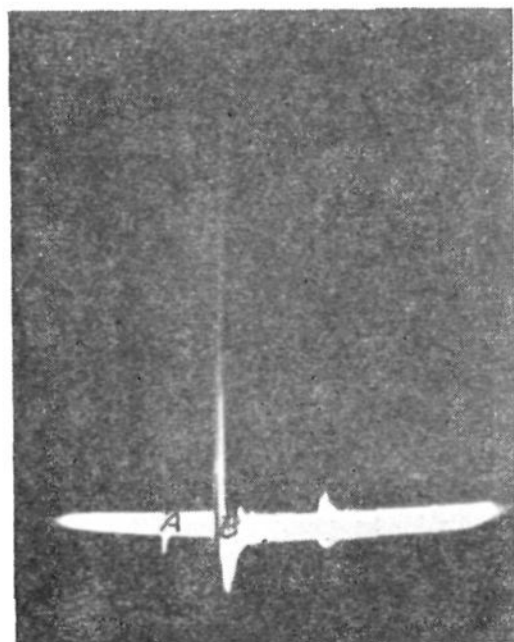


Fig. 5.—Showing the amplitude of the transmitted wave on the oscillograph.

Since there is so far no agreed mechanism of gel formation this work has been undertaken to study the problem from a physical standpoint. Details of this work on iron silicate gels and other gels of the Weimarn type will appear in forthcoming publications.

My thanks are due to Dr. R. N. Ghosh for help and guidance in undertaking this work.

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### An Apparent Reduction of Halogens by Zinc Halides in Methanol Solution<sup>1</sup>

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In the course of an investigation of the decompo-

(1) Based upon research performed under contract No. W36-039-sc-38184 for the U. S. Army Signal Corps.

sition potentials of zinc halides in methanol solution (to be published at a later date), we have observed an interesting reaction of iodine in the presence of zinc halide in methanol and of bromine in methanol solution with zinc chloride or bromide, some qualitative aspects of which we wish to report here. If separate solutions of iodine and one of the zinc halides be prepared in dry methanol and then mixed, the mixing is followed by a rapid fading of the iodine color until the solution becomes colorless. The rate of fading varies directly as the halide/iodine ratio, the total period being of the order of a few minutes, and all of the halides seem to be about equally effective.

Repetition of the experiments with solutions containing approximately 0.05% water shows an induction period of several hours followed by fading at a considerably reduced rate, the total elapsed period to a colorless solution being of the order of 24 hours or more. Tests with varying amounts of water show that water content apparently controls both length of the induction period and diminution of fading rate after reaction has started. Aeration and exposure to light seemingly have no effect upon the reaction. Replacement of the zinc halide by  $\text{AlBr}_3$ , aluminum isopropoxide,  $\text{ZnSO}_4$ ,  $\text{CdI}_2$ ,  $\text{KI}$ ,  $\text{NH}_4\text{Cl}$  and  $\text{HBr}$  appeared to give no reaction, but use of  $\text{Zn}(\text{CH}_3\text{SO}_3)_2$  produced a partial fading after about one month. Some of these latter systems may have contained small quantities of water which may account for their failure to react rapidly, but such was definitely not the case with  $\text{NH}_4\text{Cl}$  and  $\text{HBr}$ .

To obtain a further clue concerning the nature of the reaction, a solution of iodine and zinc chloride was allowed to fade completely. The resulting solution was then electrolyzed without stirring. At from 2 to 3 volts and about 1 milliamp., iodine was regenerated. Increasing the potential to 6 volts caused fading of the iodine color again, beginning at the bottom of the cell; under these conditions zinc simultaneously plated out on the cathode with evolution of gas. Fading of the iodine color under such conditions was never complete. When the potential was removed gas evolution continued, and in ten to fifteen minutes the iodine color had returned to full strength. Three hours later the solution was again nearly colorless and gas still was being evolved. On the basis of these observations it appears that the fading reaction probably involves reduction of the iodine to iodide. Electrolysis oxidizes the iodide first to iodine and then to hypoiodite or some higher oxidation state which, in presence of the zinc halide, is unstable and reverts to iodine and then to iodide with the passage of time.

The literature appears to be devoid of information which provide an explanation of the phenomena described here. Frey<sup>2</sup> refers to a reaction between zinc chloride and iodine which occurs in fibers and may be used for biological staining procedures, but no details of the reaction seem to be available. The remarkable specificity of the zinc halides in

(2) A. Frey, *Jahrb. wiss. Bot.*, **67**, 597-634 (1927).