[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE.]

THE VIBRATION AND SYNERESIS OF SILICIC ACID GELS.

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In earlier work with silicic acid gels one of us noticed a sound-producing vibration when the vessel containing a certain gel was lightly tapped. Kohlrausch[1] and Hatschek[2] made similar observations, but did not investigate the phenomenon. Evidently it was not very striking. W. E. Henderson[3] secured some vibration with a ferrous hydroxide gel.

We planned a study of the conditions affecting vibration frequency of the gel hoping to throw some light on the structure of gels, and the cause of the vibration.

The Pitch of Vibration.

A "water white" sodium silicate solution was poured into an equal volume of acid and the mixture allowed to set to a solid gel. The water glass used was free from iron and was found, by analysis, to be 1 Na_2O : 3.27 SiO_2. When diluted to a specific gravity of 1.06 it was neutralized by an equal volume of 0.54 *N* acid, using phenolphthalein as an indicator. The time of "set" varied from minutes to weeks depending on concentrations and other factors. All tubes of gels were corked to prevent drying.

Preliminary experiments with ordinary test-tubes indicated that an excellent mixture for vibration study was made by adding water glass of 1.15 sp. gr. to an equal volume of 6 *N* hydrochloric acid. This set to a solid gel in about one hour and reached its highest vibration frequency in about two days.

Before any exact measurements of pitch could be made it was necessary to standardize such conditions as diameter and length of tube. It was found that gels in tubes 8 mm. in diameter cracked badly in 3 days even though the tubes were corked. Gels in 14 mm. tubes did not crack in two weeks, this difference of behavior being probably due to the deeper meniscus in narrow tubes. We found that above a certain minimum length of gel column for each tube the pitch did not change with increase in length. In a 155 mm. test-tube this minimum length was 40 mm. With this exception extra length of tube above the gel had no effect. Tubes of wood, brass, porcelain, etc., were tried and were also found to allow vibration, but the advantage of convenience lay with glass tubes.

We finally decided to use ordinary test-tubes 150 × 17 mm. The volume of the gel mixture in each experiment was 20 cc., more than half filling the tube. When we came to measure the exact pitch of the vibra-

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[1] *Z. phys. Chem.*, **12**, 773 (1893).

[2] *Introduction to the Physics and Chemistry of Colloids*, Blakistons, 1916, 2nd edition, page 55.

[3] Private communication.

ting gels other difficulties were experienced. The quality of sound produced on tapping the tubes of gel was so different from the tone of a piano, siren or sonometer that we were unable to get accurate comparisons. Recourse was had to an old music box in which the sound was produced when metallic teeth of different length were struck on a revolving cylinder. This keyboard was readily calibrated as to the exact vibration frequency of each tooth, and produced a tone sufficiently similar in quality to that of the vibrating gels. Tuning forks would have served, but were inconvenient.

As stated above, the pitch did not vary with the length of the gel column. For example, gel columns 60 mm., 90 mm. and 120 mm. in length, but of equal diameter, vibrated, on tapping, with a frequency of 1024 per second, two octaves above middle C, indicating that the vibrations are not longitudinal. We then prepared columns of equal length but different diameters. The vibration frequency of the column 34 mm. in diameter was 341 per second; of the column 23 mm. in diameter, 640 per second; of the column 15 mm. in diameter, 1152 per second. Evidently the vibration frequency varies approximately inversely as the diameter, and consequently the vibrations are transverse.

We found that the pitch rose with increase in the concentration of the silicic acid formed. This is shown in Fig. 1, which is given in two parts for clearness. The abscissa represents the density of water glass solution which was mixed with an equal volume of 4 *N* acid. Since the water glass of 1.06 density is neutralized by an equal volume of 0.54 *N* acid the excess of hydrochloric or other acid used can be determined by subtracting the appropriate values from 4 *N*. As there was more than enough

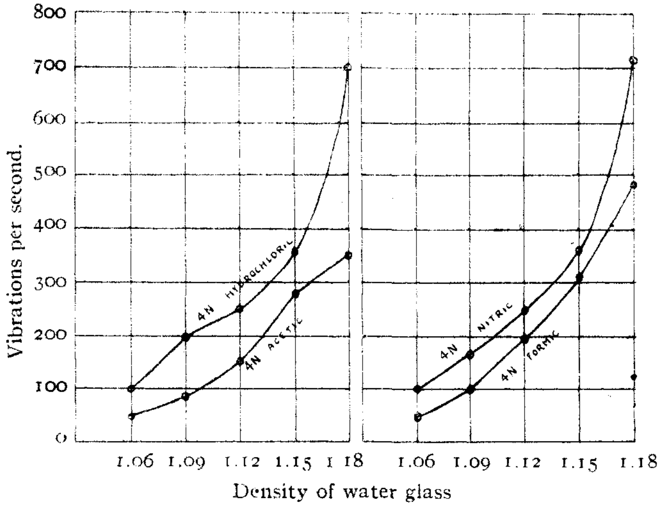

Fig. 1.—Relation of Silicic Acid Concentration to Vibration Frequency.

acid added to release all the silicic acid the curves actually represent the pitch corresponding to different concentrations of silicic acid.

It is important to note that the pitch is higher with gels made by the use of the more highly ionized acids. This fact led us to study the effect of excess hydrogen-ion concentration on a definite concentration of silicic acid. We added to water glass of 1.12 sp. gr. more than enough acid to react completely with the sodium silicate. Six samples were taken and 6 different acids used. In all experiments the actual amounts of silicic acid liberated were the same. Fig. 2 shows curves for gels involving the use of 3 organic and 3 mineral acids.

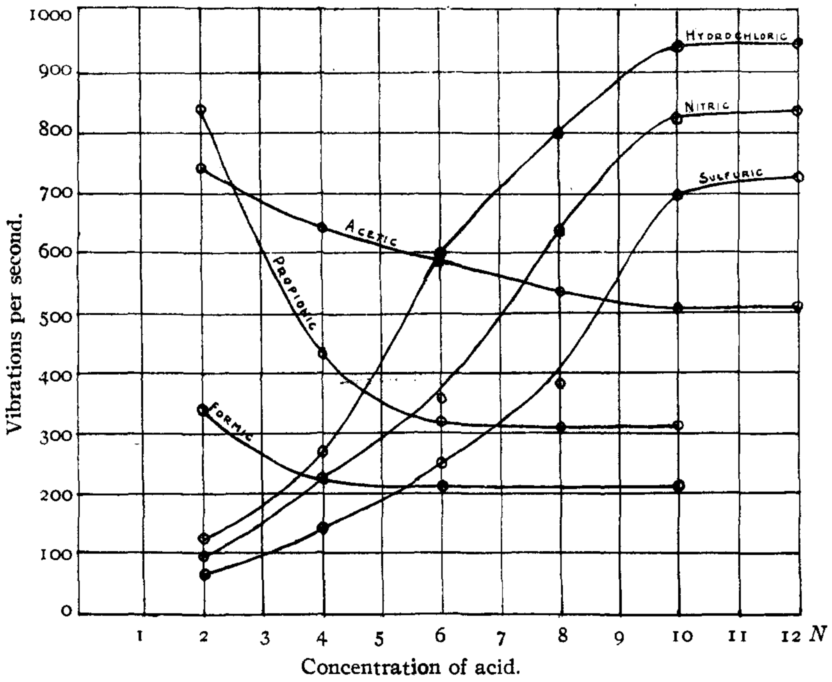

Fig. 2.—Relation of Excess Acid to Pitch of Vibration.

It is evident that the pitch rises with increase in concentration of hydrogen ion, up to a certain point, in the case of gels made by mineral acids. The pitch of sulfuric acid gels is lower at all corresponding points than that of gels made with the more highly ionized hydrochloric or nitric acids. A startling contrast is found in the behavior of gels made with organic acids. With increase in excess of acetic, propionic or formic acids the pitch falls. It is true, of course, that the sodium acetate formed in the reaction of sodium silicate with acetic acid represses the ionization of the acetic acid excess so that the hydrogen-ion concentration is less than with similar gels made with the stronger acids. This, however, does not account for the marked differences shown in Fig. 2. The repression of ionization of the weak organic acids is relatively greater with a small excess of the acid than with the gels containing a greater excess. Hence the hydrogen-ion concentration steadily increases with increase in excess of added acid. Pitch, then, does not always rise with increase in hydrogen-ion concentration.

There is, of course, an increase in the concentration of acetic acid molecules, for example, and these molecules must have a marked influence on the structure of the gel and hence on its pitch. The concentration of molecules of hydrochloric and the other strong acids is low, due to their greater ionization.

Basic gels made by mixing water glass with an amount of acid insufficient to react with all the sodium silicate vibrate with very low frequency. Neutral gels, setting almost instantly, are rather soft and vibrate with still lower frequency than the basic gels.

Rigidity of gel structure is unquestionably the main factor in sound production. Gels in thick walled tubes ring with higher pitch than gel columns of equal diameter in thin walled tubes. The total diameter of gel plus glass is greater in one case but the effect of greater rigidity of glass outweighs the effect of greater diameter.

Syneresis.

By syneresis[1] is meant the separation of water solutions from highly hydrated substances such as silicic acid gels. The breaking of custards into solid and liquid on overheating and the formation of curds and whey from milk are common examples. This phenomenon is almost universal. The subject of syneresis was introduced by an attempt to explain the vibration of certain gels. We knew that the gels vibrated as rigid solids on being struck but we also felt that they were under tension in an effort to contract. To prove this we sought to line the test-tube with some surface to which the gels could not adhere. Then if there was any tendency to contract, the gels could pull away from the walls because free to do so. The glass was coated with vaseline, paraffin, camphor, sulfur, collodion, etc., but of these vaseline was by far the best. It was melted and poured around until, on cooling, a rather thick layer formed. Gels formed in vaselined tubes contracted freely to a much smaller volume and not by mere evaporation, as the tubes were corked. A paper-thin glass bulb was filled with the gel mixture and on setting the gel contracted so powerfully that the glass caved in. In this experiment the glass was not vaselined so that the gel adhered strongly to it. Contraction was thus clearly shown, and naturally it follows that gels in glass tubes not vaselined must be under considerable tension as long as the gel adheres to the glass.

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[1] Capillary-held water is not properly included in the term "Syneresis."

But to prove that tension influenced the pitch of the vibrating gel was another matter.

The same gel mixture (water glass of 1.15 sp. gr. and 6 *N* nitric acid) was poured into a plain test-tube and also into a vaselined tube of the same diameter. On standing 8–10 days the gel in the vaselined tube had contracted so much that it could be shaken out. On tapping this gel thus removed from the tube it was found to vibrate just as did the gel under tension in the plain tube. But the vibration frequency of the gel in the tube was 1024 with a diameter of 20 mm. while the free gel had contracted to a diameter of 16.6 mm., and vibrated only 768 times per second. Since pitch varies in a general way inversely as diameter, the free gel might have been expected to yield a higher pitch, especially since its density was greater. The fact that its pitch was lower is proof positive of the importance of tension in sound production, for the greater the tension the greater the rigidity. Slight syneresis (separation of water solution) was common as gels stood, increasing with time, and when gels split syneresis became considerable. Marked syneresis quickly developed when gels stood in vaselined tubes. A gel free to contract simply squeezed out a volume of liquid equal to the decrease in volume of the gel.

To study the effect of external surface 4 bulbs, lined with vaseline, were filled with gel mixture and allowed to synerize.

TABLE I.—EXTENT OF SYNERESIS.

Volume of gel in cc.	Syneresis, volume of solution in cc.	Syneresis, in cc. to 1 cc. of gel.	Surface of spheres in sq. cm.
35	4.90	0.114	52.5
90	9.72	0.108	81.0
250	25.75	0.103	210.0
1140	87.8	0.077	285.0

Table I shows that syneresis is relatively much greater in small spheres than in the larger spheres. The phrase "specific syneresis" might be applied here. The relation of surface to volume of spheres increases rapidly as the volume of the sphere becomes small, in fact, the syneresis of spherical gels closely parallels the change in the relation of surface to volume. This is excellent proof that syneresis varies directly as the free surface. To test this theory further we poured equal volumes of gel mixture (50 cc.) into vaselined vessels such that one gel was 70 mm. wide and 15 mm. deep; a second gel, 50 mm. wide and 28 mm. deep; a third, 40 mm. wide and 40 mm. deep; and a fourth, in a narrow tube was 25 mm. wide and 125 mm. deep. The syneresis of the first was 6.6 cc., of the second 6.3 cc., of the third 5.18 cc., and of the fourth 9.2 cc. The fourth had the greatest free surface and consequently the greatest syneresis. The third had the least surface, being nearest to spherical in shape, and had the least syneresis.

We also found that increase in free surface due to cutting gashes in a gel increased the syneresis. A cube of a newly set gel was cut out from a larger mass and placed in a stoppered vessel. It synerized as great a volume of liquid as an equal volume of the same gel in a vaselined tube and 7 times as much as in an unlined tube.

The time element was very important. Syneresis began sooner with some types of gel than with others and continued for months, although at a decreasing rate. Silicic acid gels made with hydrochloric acid were slower to pull away from vaselined tubes. Out of a series of 120 tubes only 3 had completely pulled away from the vaseline in one month. Gels made with nitric and sulfuric acids pulled away in 8 to 10 days; gels made with acetic, formic or propionic acids in 10 to 15 days. The contraction was more rapid with gels of higher silicic acid concentration.

TABLE II.

Relation of Syneresis to Concentration of Silicic Acid.

Volume of Gel, 20 cc. Equal Volumes of 10 N Formic Acid and Water Glass.

Sp. gr. of water glass.	Syneresis, cc. of solution.
1.09	3.5
1.12	4.7
1.15	5.2
1.18	5.8

In Table II the 10 N formic acid was more than enough to react with all the sodium silicate so the variation in density of water glass used corresponds to a similar variation in the concentration of silicic acid formed. Similar results were obtained using 4 N acetic acid and 10 N nitric acid. With hydrochloric acid syneresis was inconveniently slow.

TABLE III.

Relation of Syneresis to Excess of Propionic Acid.

Volume of Gel, 20 cc. Equal Volumes of Propionic Acid and Water Glass of 1.12 Sp. Gr. Used.

Normality of propionic acid.	Syneresis, cc. of solution.
2	5.4
4	2.9
6	2.7
8	2.3

Water glass of 1.12 sp. gr. required an equal volume of N acid to neutralize it, so the gels made as in Table III contained the same concentration of silicic acid. With increase in the excess of propionic acid syneresis decreased. Similar results were obtained by the use of citric and formic acids. Very different results were obtained using nitric acid. With increase in the excess of nitric (or other mineral acid) syneresis increased.

This difference accords well with the different effects of organic and mineral acids on the pitch of vibration. The depressing effect on both pitch and syneresis exerted by organic acids can be due only to the molecules of the acid. Were it merely a function of hydrogen-ion concentration trichloroacetic acid should produce gels of higher pitch and greater syneresis than gels from the less ionized acetic acid. Such was not the case.

TABLE IV.

10 cc. of Water Glass (1.15 Sp. Gr.) Mixed with 10 cc. of 3 *N* Acid. Time, 2 Weeks.

Acid.	Vibration frequency.	Syneresis, in cc. of solution.
Acetic	682	4.7
Monochloroacetic	427	4.4
Trichloroacetic	320	2.2

It is clear from Table IV that un-ionized molecules of trichloroacetic acid have a greater influence on the rigidity and contraction of silicic acid gels than have the un-ionized molecules of acetic acid.

The neutral gels studied gave but little syneresis. Interesting results were obtained with basic gels. Very basic gels set with extreme slowness and were unsuitable. On setting they do not "bind" all the water but coagulate as a soft layer. Moderately basic gels set in solid form and then separate very large volumes of water solution. After standing two months a gel made from 10 cc. of water glass of 1.18 sp. gr. and 10 cc. of *N* acetic acid separated 18 cc. of solution, the gel having contracted to a volume of 2 cc. This was not a case of drying out for the shriveled gel was immersed in the solution. As in all experiments, the tube was corked.

Many other gels could be studied with respect to pitch and syneresis. For example, a gel made with equal volumes of water glass, of 1.15 sp. gr., and 3 *N* citric acid had a vibration frequency of 1024, two octaves above middle C. A very slightly basic gel of this type made with water glass of 1.[illegible] sp. gr. and 0.8 *N* citric acid showed marked syneresis. Neutral gels in general had very low vibration frequency.

A very beautiful tone was produced from a heavy-walled pint milk-bottle half full of a gel made with water glass of 1.15 sp. gr. and 6 *N* hydrochloric acid. On holding this bottle lightly by the top and swinging it sharply against a wooden table, or similar object, overtones could be detected. The water (of syneresis) on the surface was thrown into a wave pattern and drops splashed against the stopper.

Summary.

1. Vibrating silicic acid gels were made which on tapping produced a tone two octaves above middle C.

2. Such gels vibrate as rigid solids, but tension is an important factor. That they are under considerable tension is proved by their great contraction in vaselined tubes.

3. Contracted gels removed from vaselined tubes have a lower vibration frequency than similar gels adhering to the walls of tubes of equal

diameters. Since vibration frequency varies inversely as the diameter of gel column, tension must exert some influence on pitch.

4. Vibration frequency varies directly as the concentration of silicic acid, increases with excess of mineral acids, but decreases with excess of organic acids.

5. Syneresis increases with increases in concentration of silicic acid, increases with excess of mineral acids, and decreases with excess of organic acids. For acid gels the same factors that increase vibration frequency (by increasing tension and thus effective rigidity) also increase syneresis. Vibration and syneresis have a direct relation to tension. Basic gels are somewhat abnormal in this respect.

6. Syneresis (separation of water solution from gels) varies directly as the free surface. When gels contract in vaselined tubes far more liquid separates than from equal volumes of gel in plain tubes to which the gel adheres.

7. The extreme in syneresis was observed with moderately basic gels. The solution synerized was as much as 90% of the volume of the gel in some instances.

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THE VAPOR PRESSURE OF TETRANITRO-METHANE.[1]

By Alan W. C. Menzies.

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The measurements in a portion of the range here reported were made in 1918 at the request of the Division of Chemistry and Chemical Technology of the National Research Council, and were desired for purposes connected with the war. Because such data have a permanent value, however, it was thought desirable to extend the measurements over a considerably wider range than was called for at that time.

The sample of tetranitro-methane furnished for the work, about two cc., was somewhat small for effective purification by fractionation. Its boiling point was found to be 125.7° under 760 mm. pressure, however, which is in close agreement with the reported values of Schischkow[2] and of Chattaway,[3] both of whom, from independent observations, obtained 126° as the normal boiling point. Berger[4] states that the boiling point of his, apparently less homogeneous, preparation was 124–125° under 750 mm. pressure; and this corresponds to temperatures 0.4° higher at 760 mm. In spite of this concordance in boiling point, the possibility of impurity remains the chief uncertainty in the data here recorded; and it is therefore superfluous to elaborate details of the measurements.

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[1] N. R. C. War Problem No. 142.

[2] *Ann.*, **119**, 248 (1861).

[3] *J. Chem. Soc.*, **97**, 2099 (1910).

[4] *Bull. soc. chim.*, [4] **9**, 26 (1911).