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SILICIC ACID.

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The relations of silica and water in the so-called silicic acids and the silica gels, and the mechanics of the solution of silica by water, are problems which for many years have received a great deal of thought by chemists and geologists. The following experiments, which have been extended over a period of years, have been carried out largely to obtain a better knowledge of the relations that silica and water bear to each other.

Effect of Fine Grinding on Silica.¹

The starting material was Ottawa sand containing over 99% of silica. It was ground for 400 hours by means of large rounded pieces of quartz in an Abbe ball mill. This period represented the actual time of grinding, although the attendant operations and the grinding were conducted daily for several months. Great care had to be taken to prevent caking. The average fineness of the ground material was no more at the end of 400 hours than it had been at the end of 350 hours; and by evaporating in platinum with hydrofluoric and sulfuric acids it was found to contain 98.72%, showing that a slight amount of impurities had been introduced from the grinding apparatus. Measurements were made of the size of the ground silica particles by placing samples on a glass slide, moistening with water and covering with a cover glass. The samples were then examined with a microscope with a calibrated ocular and showed that 85% of the material had a diameter of less than 0.004 mm., while 15% was between 0.004 and 0.016 mm. in diameter.

This finely divided material was shaken up with 500 cc. of conductivity water and allowed to settle at room temperature in tall, glass-stoppered cylinders. W. Machaelis in a paper read before the German Portland Cement Manufacturers on March 9, 1909, states that quartz reduced to an impalpable powder by prolonged grinding becomes so active that boiling with water will convert it into colloidal hydrated silicic acid. When the heavier particles had completely subsided and the supernatant liquid appeared homogeneous but not completely transparent, the liquid was examined by evaporation of 100 cc. portions to dryness in a platinum dish and the residue volatilized with hydrofluoric and sulfuric acids. The results of this procedure indicate that in from 2 to 3 weeks silica to the extent of 0.028 to 0.032 g. per liter remains permanently in solution.

When first shaken with water the ground silica forms a mechanical suspension and a large part of the suspended matter settles quickly. In a short time the finer particles form strata which at the end of about 10 days disappear and at the end of 15 days the solution is stable.

¹ With G. G. Town.

Colloidal Character of the Silica in Water.

When viewed with the ultramicroscope the fine particles which remained suspended in the water, after the ground silica had been shaken and the whole allowed to settle for several weeks, showed a rapid Brownian movement.

When a powerful beam of light was passed through the liquid in a beaker the exhibited Tyndall effect was produced.

These experiments show that if quartz is ground sufficiently long, it can be so finely divided that it will go into colloidal condition when treated with water.

From the rate that the particular material worked with settled out from water, it would seem that up to 2 weeks the whole is a more or less coarse suspension which slowly settles and finally leaves a stable colloid.

Experiments on Fine Grinding of Orthoclase.¹

Carefully selected orthoclase was ground for 388 hours in an Abbe ball mill. The mill was opened daily and the caked material dislodged. This material was shaken up with water and allowed to settle in the same way as has been described with quartz. An additional experiment was conducted by shaking the finely ground feldspar with alcohol. After settling, both the alcohol liquid and the water liquid of the orthoclase showed the Brownian movement when observed with the ultramicroscope and also gave the Tyndall effect. The water suspension was filtered through a Chamberlain F. filter and was then optically empty, but when filtered through an acid-hardened filter paper,² it showed particles which exhibited the Brownian movement. This should fix the size of the particles as between 4μ and 1.3μ .

Samples of this extremely finely powdered feldspar which had been suspended in alcohol for a short time were decanted, and the alcohol evaporated off and heated in an autoclave with water. One g. portions of this material, heated with 100 cc. of water in a platinum dish, for 3 hours at 168° , corresponding to 50 kg. steam pressure, showed an alkalinity against 0.1 *N* hydrochloric acid equivalent to less than 0.5% of K_2O , indicating that only a small portion of the feldspar had actually gone into true solution.

Action of Water at Elevated Temperatures on Quartz.

As is known to those who have worked with water in glass and siliceous material of various kinds at high temperatures and pressures gelatinization takes place. From the many experiments with silica and water which have been conducted in this laboratory, it would seem that the first thing which takes place when silica is wet is hydration. Some of the silica

¹ With G. G. Town.

² Schleicher and Schüll, No. 602.

then passes into solution and if allowed to remain in contact with water will finally reach the solution equilibrium shown by Lenher and Merrill.¹ Along with this process of hydration and true solution that portion of the silica which is sufficiently fine goes into the colloidal condition. When the temperature is raised this hydration takes place so rapidly that it can be readily followed.

At 400° in the sealed high pressure bombs of Morey, water will slowly gelatinize all of the fused quartz or silica ware on the market to-day. At 500° water will slowly cause the gelatinization of transparent quartz crystals. The resulting silica gels differ widely in character, depending on the temperature and pressure, and also on the original quartz used. Some of the gels when air-dried go to a loose, finely divided powder; others dry into concentric layers and into fairly adhering compact plates.

Some recent experiments made by G. R. Shaw² show that certain fused quartz tubes, when heated to about 500° with water in a bomb, on cooling give evidence of recrystallization on the sides of the tubes. Numerous fragments were noted which under the polarizing microscope showed optical activity and also showed hexagonal structure.

Some preliminary experiments made by O. J. Noer with the finely ground quartz prepared by G. G. Town seemed at first sight to be very significant. At 100° in a bomb, water hydrates this ground material in a manner which appeared to be definite. A number of experiments seemed to show by *analysis* that metasilicic acid, H_2SiO_3 , was formed, the results of various experiments agreeing to within a few hundredths of 1 per cent. and agreeing exactly with the theoretical percentage requirements of the formula H_2SiO_3 . However, the material which to the naked eye appeared homogeneous, when examined under a polarizing microscope proved to be far from homogeneous. In reality it consisted of the broken fragments of the original quartz, interspersed with masses of gelatinous silica; it was, therefore, not metasilicic acid, but a physical mixture of silica gel and quartz. This hydrated material when allowed to dry spontaneously in the air hardened to a compact coherent mass which in texture, hardness and general appearance much resembled quartzite.

The action of water at various temperatures and pressures on silica and on silica gels has been studied by Walter T. Schrenk³ in considerable detail. Several hundred experiments were made in a Morey bomb at temperatures which varied in the individual experiments from 300° to 600° and the lengths of time of the experiments varied from 8 hours to 312 hours. The experimental difficulties to be overcome in work of this character have been almost insurmountable. While thus far it has been impossible to obtain the quantitative measurements that are desirable, it can be said in general that the extremely finely ground quartz previously described hydrates at 300° to 450° in presence of excess of water to a gel containing 15 to 18% of water. On the other hand, silica gels

¹ Lenher and Merrill, THIS JOURNAL, 39, 2630 (1917).

² Of this laboratory.

³ This laboratory.

made by the dialysis of the sodium silicate-hydrochloric acid mixture and containing 2.33% of silica, the remainder being chlorine-free water, when heated from 300° to 600° in the bomb with great excess of water, lose water, and in from 8 to 312 hours yield a product containing approximately 20 to 30% of silica and 70 to 80% of water.

Effect of Pressure on Silica Gels.¹

The salts of orthosilicic acid, H_4SiO_4 , and of metasilicic acid, H_2SiO_3 , are found among some of our best known silicate minerals. The free acids themselves are compounds that have plenty of analogs in the fourth group of the periodic system of which silicon is a member. Our common sodium silicate itself is a substance whose composition depends entirely on the quantities of reacting substances used in its original formation.

A very suggestive method described for the formation of orthosilicic acid is that of Norton and Roth.² Their method of producing gelatinous silicic acid by passing silicon tetrafluoride into water, is considered by them to be a method particularly desirable in order to obtain the material free from non-volatile foreign matter. They washed the gelatinous mass with water on a cloth filter and allowed it to drain a short time, after which the water was removed by ether or benzene. The washed acid was then squeezed in a vise and an orthosilicic acid of constant composition reported as a definite body.

In our studies with silica these particular experiments seemed of sufficient promise to follow out in more detail. The particular points which looked attractive were a study of the effects of various and measured pressures on silica gels. If silica gels can be dehydrated by pressure from the condition of a high degree of hydration to the definite hydrate of the formula H_4SiO_4 , it would seem that by using various pressures it should be possible to plot a curve showing the relation between pressure applied and the water remaining with the silica.

For the preparations of gelatinous silica it was most convenient for us to hydrolyze pure silicon tetrachloride. The gel was washed with water until free from chlorides, after which the excess of water was removed by squeezing the product between cloths by hand. The gel at this stage contained between 80 and 90% of water and was preserved in a glass-stoppered bottle for use.

In place of the vise used by Norton and Roth, who could in this device obtain only about a hundred kg. pressure per square inch, a Riehle testing machine was used. By means of a machine of this kind it is possible to obtain a compression of 45,400 kg. to the square inch and to apply any particular pressure up to 45,400 kg. that is desirable.

¹ With Andrew J. Snyder.

² Norton and Roth, *THIS JOURNAL*, 19, 832 (1897).

In the first experiments, comparative low pressures were used. 230 kg. pressure, which is probably what a good vise would give, gave a mass which contained 77.7% of water; 340 kg., 71 to 73% of water; 454 kg., 68.5 to 71% of water; 680 kg., 50 to 67.5% of water; 900 kg., 46.5 to 53.5% water; 1,800 kg., 51-52% water. In these experiments the gels were pressed between sheets of Whatman's filter paper, but at pressures of 2300 kg. and upwards, the adherence of the product to the paper became so pronounced that it was found necessary to use a canvas filter cloth as the medium to absorb the water. With 4540 kg. pressure the water retained by the silica was from 57 to 60%. At pressures from 4540 to 13,600 kg. various combinations of canvas filter cloth and hardened filter paper with copper foil gaskets were used. The water content then dropped down to 44.5% at both 9000 and 13,600 kg. At 13,600 kg. 2 sheets of heavy rubber were also tried as a support for the gel but 55% of water still remained. In another series of experiments a laboratory diamond steel mortar was used at pressures of 11,600 and 13,600 kg. with the results that about 30% of water remained. The results obtained with the diamond steel mortar were so encouraging that it was decided to use tool steel plates.

Two carefully faced round steel plates 100 mm. \times 12.5 mm. were used and as the water was squeezed out of the gel, the free water was removed by means of filter paper. The amounts of water remaining with the silica was of the same general order as with the other devices employed. The product in each case, after being pressed, looked, in the ordinary sense of the word, dry. Using the tool steel plates a pressure of 44,600 kg. was attained, yielding a product which retained 34 to 35% water.

In order to continue the experiments at still higher pressures, 2 special chrome-nickel-steel plates kindly furnished us by Dr. Geo. W. Sargent of the crucible Steel Company of America, were carefully machined in such a manner that their contact surfaces were parallel to within 0.00508 mm. From the contact surface to the outer edge of the disks they were slightly bevelled to take up the flow of the steel at very high pressures. These plates withstood the pressure of 272,700 kg. very well and the results obtained were fairly constant. A Tinius Olsen hydraulic press was used to obtain this high pressure. The product obtained showed a water content of 12.3 to 12.9%, which closely approximates the ratio of one molecule of water to 2 of silica, corresponding to the formula $H_2Si_2O_5$. The final product was a white amorphous powder, which under the microscope showed no crystalline structure.

A number of the gels, after being pressed to 272,700 kg., were transferred to desiccators and allowed to stand for various periods of time. The material which was approximately 2 molecules of silica to one of water actually contained 12.5% water, and in 2 months desiccation over phos-

phorus pentoxide lost 5.75% of water, but still retained 6.75%; while the material which was dried further over calcium chloride retained at the end of 2 months 9.24% of water. Longer desiccation would doubtless remove more water.

From the results obtained by submitting gelatinous silica to the successively high pressures studied, should it be possible to press a silica gel more strongly than has been done, it seems probable that more and more water would be removed as the pressure increased.

From the observations made by Lenher and Merrill,¹ it is obvious that silica possesses a very definite solubility in water.

When quartz is ground sufficiently fine, pure water alone will cause it to go into the colloidal state as has been verified by actually finding it to be a colloid. Additional evidence of the fact that fine grinding alone can subdivide a substance so finely that water will cause it to go into colloidal form, is afforded by the fact that orthoclase when ground extremely fine goes into the colloidal form in exactly the same general manner as does silica itself.

The action of water on silica is therefore that of a solvent, to produce the silica gel, and to cause it to go into the colloidal form. The more finely divided the silica the more rapid is the action. This action of water on silica with the subsequent hydration is accelerated by heat and with water under high pressures, such as are obtained in the steel bombs, the hydration of large-sized quartz crystals or even fused quartz can be readily followed.

The silicic acids themselves are purely hypothetical. While their salts form our common silicate minerals, the acids in free condition have never been prepared. The so-called "silicic acid" and the gels which are so common should therefore be regarded as corresponding to the general formula $XSiO_2YH_2O$ in which the quantities of water and silica can vary from a true solution of silica in water, successively through the highly hydrated gels which pressure alone will convert from a water content of nearly 98% to a silica which contains only a few per cent. of water.

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¹ *Loc. cit.*