The Chemistry of Silica Surfaces.

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[Reprint Order No. 5820.]

Solubility measurements indicate that an incomplete monolayer normally exists on silica surfaces which is more soluble than the rest of the material. This layer has been identified as silicic acid by following the exchange reaction between a quartz surface and dissolved [^{31}Si]silicic acid. The layer is removed by sodium hydroxide and re-formed when the silica is equilibrated with a silicic acid solution.

Lenher and Merrill (*J. Amer. Chem. Soc.*, 1917, **39**, 2630), using platinum apparatus, found that the solubility of gelatinous silica at 25° is 16·2 mg. and at 90° is 41·8 mg. of SiO_2 in 100 ml. of conductivity water. The solute was estimated gravimetrically. Equilibrium between the gelatinous silica and water was established after about 8 days at 25° and after 24 hours at 90°. Lenher and Merrill found that ignition of this silica reduced the rate of dissolution but concluded that " the true solubility of ignited silica is probably the same as that of gelatinous silica, but as saturation is not reached in any short period of time, the apparent solubility is somewhat less than that of the gelatinous silica." Alexander, Heston, and Iler (*J. Phys. Chem.*, 1954, **58**, 453) recently re-examined the values for the solubility of silica in water. Measuring the solute concentration by a colorimetric method, they found that amorphous silica produced by the combustion of silane, wet silica gel, and sols produced by treating sodium silicate with cation-exchange resins all had the solubility, 10—14 mg./100 ml. at 25°.

The values found for the solubility of quartz and other forms of silica are mostly much lower than Lenher and Merrill's values for silica gel; for example, Briscoe, Matthews, Holt, and Sanderson (*Trans. Inst. Min. Met.*, 1936—37, **46**, 291) found that, when 1 g. of quartz dust was shaken with 100 ml. of water at 20°, the solute contained only 1·6 mg. of SiO_2 per 100 ml. after 50 days. Other observers give widely differing values (see King and Belt, *Physiol. Rev.*, 1938, **18**, 329).

The rates of dissolution of various forms of silica have also been studied (see, *e.g.*, Briscoe, Holt, Matthews, and Sanderson, *loc. cit.*; Lucas and Dolan, *Canad. Med. Assoc. J.*, 1939, **40**, 127). It is generally agreed that, when powdered silica is added to water and the concentration of the dissolved silica is plotted against time, the curve shows an initial phase of rapid dissolution after which the silica dissolves much more slowly. If the extraction is continued for a number of days, in which saturation would be assumed, the concentration of the dissolved silicic acid depends upon the mass of silica extracted and the size of the particles. This initial rapid dissolution was also demonstrated indirectly by Benton and Elton (*Trans. Faraday Soc.*, 1953, **49**, 1213), who, when measuring ionic absorption energies, noted a rapid increase in the conductivity on adding powdered silica to water.

Kitto and Patterson (*J. Ind. Hyg. Toxicol.*, 1942, **24**, 59) attributed the initial rapid solubility of quartz to the presence of surface imperfections and to a disturbance of the surface caused by abrasion, likening the surface to the Beilby layer found on polished metals. This theory has been adopted more recently by Clelland and Ritchie (*J. Appl. Chem.*, 1952, **2**, 42), who estimated that the layer was between 0·02 and 0·15 μ thick, and by Nagelschmidt, Gordon, and Griffin (*Nature*, 1952, **169**, 538). Heavens, however (*Acta Cryst.*, 1953, **6**, 571), obtained sharp Kikuchi patterns in electron-diffraction photographs of the surface of a freshly fractured and an acid-washed quartz crystal, proving the absence of any thick layer of non-crystalline material. It is difficult to reconcile the fact that the abnormal solubility phenomena are shown by powdered fused silica with a theory which postulates organized and disorganized layers.

Lucas and Dolan suggested that the initial rapid dissolution was due to trace impurities such as alkali metals. Rapid dissolution from sharp corners and protruding edges was also suggested as the cause (Jötten and Pfefferkorn, *Arch. Hyg.*, 1953, **137**, 79). These theories are improbable, however, since it has been established that powders may still show the unusual solubility characteristics after repeated extraction with water. A microscopic examination of some samples used for solubility determinations revealed insufficient small particles to account for the mass which dissolved rapidly.

We have sought further evidence to explain the anomalous solubility characteristics of silica by studying the rate of dissolution of powders and the effect of these powders on silicic acid solutions, and by observing the exchange phenomena which occur between solid silica and radioactive silicic acid sols.

Study of the process is complicated by polymerization of the dissolved silicic acid, which occurs most rapidly at pH 5·5—6 (Treadwell, *Trans. Faraday Soc.*, **1935**, **31**, 298). Polymerization is much slower in more alkaline or more acid solutions. Our experiments were made primarily at high pH values at which polymerization was negligible. In most experiments buffers were not used since those acting over the alkaline pH range all interfere with the silicomolybdate reaction, the basis of the only colorimetric methods available for the estimation of silicic acid in low concentrations. Borate and acetate buffers were used for some experiments.

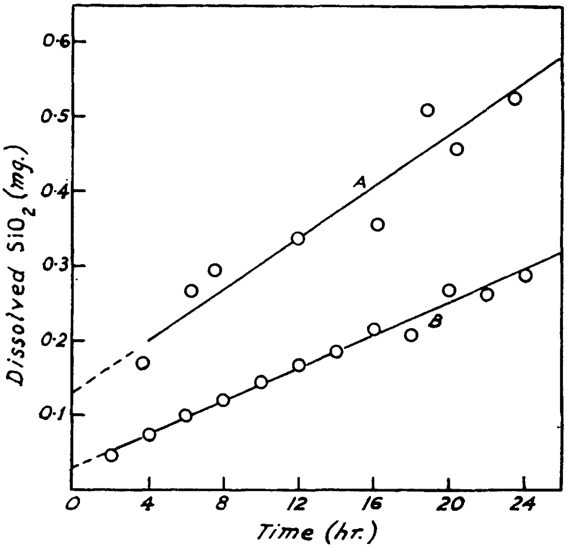


FIG. 1. *Rate of dissolution of silica powder in* 0·1N-*sodium hydroxide.*
(*A*) Original powder.
(*B*) Alkali-extracted powder.

Earlier workers emphasized a relation between particle size and mass (*i.e.*, surface area) of the silica powders and their rate of dissolution. Surface areas of all the powders were measured both by the method of projected areas and by nitrogen adsorption. On the silica powders used, these two methods gave values which differed by a factor of about 4. The values given by the nitrogen-adsorption method are probably more relevant. The silica powders were graded in size by water elutriation so that very small particles should not unduly affect the rate of dissolution. "Polythene" apparatus was used to prevent contamination of the solutions by silica derived from glassware.

Solubility–Time Curve of Silica Powders.—The rate of dissolution of a silica powder (2 g.) in 0·1N-sodium hydroxide (15 ml.) is shown in Fig. 1, curve *A*. Initially, dissolution is rapid but later is slow, the concentration–time plot being linear. Linear extrapolation of the curve shows that the mass of silica which dissolves rapidly is 0·13 mg. of SiO_2 per g. of powder.

The powder from this extraction was separated centrifugally, washed free from alkali, then dried at 120°. The rate of dissolution of this sample in 0·1N-sodium hydroxide is shown in Fig. 1, curve *B*, which lies below the previous curve, and, by extrapolation, the mass of silica which dissolves rapidly is only 0·03 mg. of SiO_2 per g. of powder.

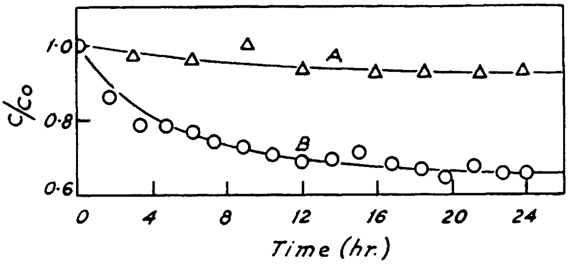
These observations suggest that on the surface of the silica there is material which is easily dissolved, and from solubility and surface-area measurements obtained on two samples it is possible to estimate the extent of this layer, assuming that it is silicic acid and is present as a monolayer. To calculate the values given in Table 1, an area of 12·3 Å^2 has been assumed for the silica unit. The measurements of surface areas made by nitrogen adsorption suggest that about one-sixth of the surface is covered.

TABLE 1.

Powder	Wt. of layer (mg./g.)	Surface area (m.^{2}/g.) (*a*) Optical	Surface area (m.^{2}/g.) (*b*) N$_2$ adsorption	Fraction of surface covered by monolayer, calculated from : (*a*)	Fraction of surface covered by monolayer, calculated from : (*b*)
A	0·10	0·22	0·9	0·56	0·14
B	0·13	0·26	1·0	0·62	0·16

Adsorption of Silicic Acid on Silica Surfaces.—Further evidence for the presence of the surface layer was obtained by studying the effects of silica powders on silicic acid solutions. A silicic acid solution was prepared containing 10 mg. of SiO$_2$ in 100 ml. of solution in borate buffer, at pH 8, this concentration being well below that of a saturated solution as determined by Lenher and Merrill (*loc. cit.*) and equal to the lowest experimental value given by Alexander, Heston, and Iler (*loc. cit.*). A sample of the original silica powder was placed in this solution, and an equal weight of the alkali-extracted powder was placed in a similar volume of the same solution. The effect of the two powders on the concentrations of the silicic acid solutions is shown in Fig. 2. The original powder produced only a very small change in the concentration of the silicic acid solution (curve *A*) but the alkali-extracted powder adsorbed 0·12 mg. of SiO$_2$ from 100 ml. of solution. This result suggests that the layer present on a silica surface which is removed by alkali is adsorbed silicic acid, and that the layer is re-formed when an alkali-washed silica surface is treated with a silicic acid solution.

FIG. 2. *Adsorption of silicic acid from solution on to the original silica powder (curve A) and on to the alkali-extracted powder (curve B). The change in the concentration of the solute is denoted as the ratio of the concentration (c) after a measured time to the initial concentration* (c_0).



The silica powder was recovered from the last experiment and its solubility in 0·1N-sodium hydroxide was followed. The rate curve is shown in Fig. 3. The later portion is approximately linear, and linear extrapolation shows that the mass of silica which dissolves rapidly from 1 g. of powder is almost identical with that adsorbed from the silicic acid solution. Moreover, the rate of solution after the adsorbed layer has been removed is almost identical with that of the alkali-washed material (Fig. 1). Calculations based on the surface area measured by nitrogen adsorption show that the adsorbed silicic acid, if present as a monolayer, covers a fraction of 0·16 of the silica surface.

Exchange between Adsorbed Silicic Acid and Dissolved Labelled Silicic Acid.—The results described suggest that surface adsorption occurs from silicic acid solutions on to silica surfaces. The adsorbed silicic acid may be able to exchange with dissolved silicic acid. The original silica powder (6 g.) and the alkali-extracted powder (6 g.) were placed in solutions of radioactive silicic acid (8 ml.). The changes in the total concentration of dissolved silicic acid, measured colorimetrically, and in the concentration of the radioactive silicic acid, were followed. This experiment was performed at several pH values. When the original silica powder was added to a radioactive silicic acid solution at pH 8 or at pH 9 the concentration of the dissolved ^{31}Si fell, equilibrium being established after about 4 hours (Fig. 4, curve *A*). The total concentration of dissolved silicic acid, measured colorimetrically, remained approximately constant (Fig. 4, curve *B*). When the experiments were carried out at pH 4 or pH 5 the concentrations of both the ^{31}Si and the molybdate-reactive silicic acid remained constant. Fig. 5 shows the results obtained at pH 4. Exchange can occur, then, in alkaline but not in acid solutions, suggesting that only the silicate ion can take part in the exchange reaction.

An alkali-extracted silica powder (2 g.) adsorbed silicic acid from a solution (8 ml.) at pH 8. In this case the reduction in the concentration as shown colorimetrically was identical with the reduction indicated by the tracer technique, showing that adsorption had occurred (Fig. 6). When the alkali-extracted silica was treated with silicic acid solution at pH 8, the resulting powder would exchange with dissolved radioactive silicic acid. Thus, when 5 g. oft he alkali-extracted powder used in the last experiment were equilibrated with a silicic acid solution, then transferred to a solution of isotopically-labelled silicic acid, the ratio of the final to the initial concentration of dissolved silicic acid increased slightly to 1·1 during 8 hr. but the ratio as measured by the tracer technique fell to 0·61. This indicates that there was 0·12 mg. of SiO_2 per g. of powder which would exchange with dissolved silicic acid, a value very close to that found for the original powder.

FIG. 3.

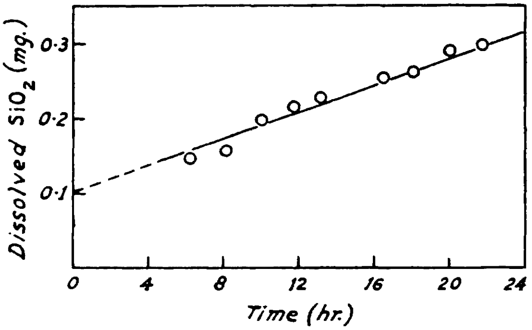


FIG. 4.

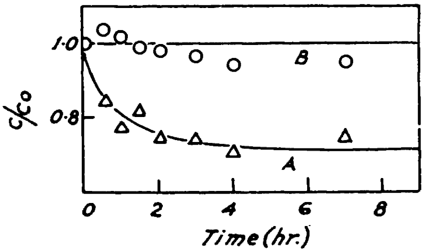
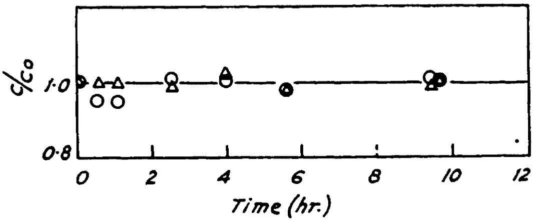


FIG. 3. *Rate of dissolution of a silica powder in* 0·1N-*sodium hydroxide. This powder was first extracted with sodium hydroxide then equilibrated with silicic acid solution before the solubility was followed.*

FIG. 4. *Alteration in the concentration of* [^{31}Si]*silicic acid* (*curve A*) *and total silicic acid* (*curve B*) *on adding the original silica powder to a silicic acid solution at* pH 8. *For c and c_0, see Fig.* 2.

FIG. 6.

FIG. 5.



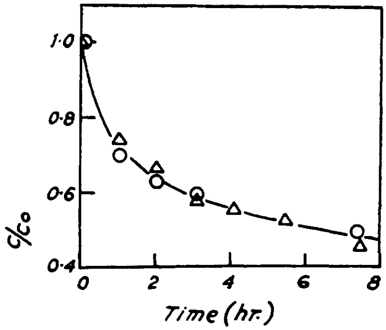


FIG. 5. *Alteration in the concentration of* [^{31}Si]*silicic acid* (Δ) *and total silicic acid* (○) *on adding the original silica powder to a silicic acid solution at* pH 4. *For c and c_0, see Fig.* 2.

FIG. 6. *Alteration in the concentration of* [^{31}Si]*silicic acid* (Δ) *and total silicic acid* (○) *on adding the alkali-extracted silica powder to a silicic acid solution at* pH 8. *For c and c_0, see Fig.* 2.

These results show that silica surfaces will adsorb silicic acid and that the adsorbed layer is identical with the " high solubility layer " which has been widely investigated. The layer is removed by alkali and is re-formed by adsorption from silicic acid solutions even if the concentration is well below that of a saturated solution. The published solubility–time curves of quartz may be dissected into two portions. The first, the " high solubility phase," is due to the dissolution of the adsorbed silicic acid layer, and the second portion represents the attack of water on the true silica lattice. The latter is very slow and the rate depends largely on the pH; preliminary results indicate that the rate at pH 14 is approximately 100 times that at pH 4.

When silica powder is added to water, any adsorbed silicic acid will dissolve rapidly at first until the rate of dissolution becomes equal to the rate of adsorption. An equilibrium will not be established in any short time unless the mass of adsorbed silicic acid is sufficient to saturate the solution : thus Alexander, Heston, and Iler (*loc. cit.*), when determining the solubility of a very finely divided amorphous silica, found that the " solubility of this silica was relatively independent of the mass, ***except when less than*** 0·1% ***silica powder is present*** in the dispersion." If it is assumed that the proportion of the surface covered by adsorbed silicic acid was the same as for our samples, the mass of silica in the adsorbed layer can be calculated from the given surface area (B.E.T.) values to be approximately 31 mg. of SiO_2 per g. of powder. The adsorbed silicic acid on 0·1 g. of the powder would then be 3·1 mg., representing a solution concentration of 3·1 mg. of SiO_2 per 100 ml., a lower value than the total solubility found by Alexander *et al.* (10—14 mg./100 ml.) but, in view of the assumptions made, a value of the right order. The powder, produced by combustion of silane, had an extremely small particle size and it was extracted for 20 days. The dissolution of silica from the lattice may have contributed appreciably, therefore, to the measured solubility.

It is apparent that the amount of silica which passes rapidly into solution in this way will depend on the surface area presented by the powder and also on its previous history. The measurements of " solubility " previously made at pH values near neutrality will represent mainly the extent of the adsorbed silicic acid layer on the surface of the particular silica powder which was used. There is, then, no justification for the statement (Alexander, Heston, and Iler, *loc. cit.*) " it is well known that amorphous silica is more soluble than crystalline silica (quartz)." The equilibration of quartz with water has never been accomplished, at least at neutrality and at normal temperatures. The dissolution of quartz requires the attack of water on the silica lattice. The kinetics of this reaction have not been studied at normal temperatures, and the rate of dissolution will depend on the surface area of the sample of quartz, but some idea of the time required for equilibration may be obtained from the curve published by Briscoe *et al.* (*loc. cit.*). Linear extrapolation of that part of the curve which represents the slow solubility phase indicates that the time required for equilibration in this case is considerably in excess of ten years.

In a number of communications both the curves representing the rate of solution of silica powders and the particle diameters were given. If it is assumed that the fraction of the surface covered by the silicic acid monolayer was the same in these dusts as in ours, it is possible to calculate the specific surface of the dust from the mass of silica which dissolved rapidly. These values may be converted into average particle diameters by assuming that the surface area–particle diameter relation is the same in all the powders and measuring this relation for a silica powder. The observed and calculated diameters are set out in Table 2. The divergence between the calculated and the observed values increases as the particle size decreases. This is probably due to uncertainty in the optical estimation of the diameter of very small particles. According to our results, these samples must have contained particles which were below the limit of resolution of the optical microscope.

TABLE 2.

	Particle diameter (μ)			Particle diameter (μ)	
Author *	Obs.	Calc. from hydrated layer theory	Author *	Obs.	Calc. from hydrated layer theory
1	1—3	1	5	0·2—0·5	0·13
2	1—3	0·25		0·33	0·13
3	5—7	2·6		0·27	0·09
	0·5—3	0·3		0·27	0·06
4	2—5	2		0·25	0·03
	0·02—0·06	0·02	6	50—200	95

* (1) Briscoe, Holt, and Sanderson, *loc. cit.* (2) King and McGeorge, *Biochem. J.*, 1938, **32**, 417. (3) Lucas and Dolan, *loc. cit.* (4) King, *Occup. Med.*, 1947, **4**, 26. (5) Kitto and Patterson, *loc. cit.* (6) Clelland, Cumming, and Ritchie, *J. Appl. Chem.*, 1952, **2**, 31.

In view of these results, much of the work which has been carried out on silica surfaces would bear re-examination and re-interpretation. A surface can be regarded as silica only if it has been pre-treated with alkali. Even then, some degree of dissolution of silica and readsorption of silicic acid may occur if the sample is dried. When powders are not pre-treated, the observed properties are those of a mixed surface of silica and silicic acid.

The polymerization of silicic acid is usually regarded as a process of condensation : "All silica and silicate structures are derived by linking SiO_4 tetrahedra . . . similar principles should be applied to the constitution of colloidal silica" (Carman, *Trans. Faraday Soc.*, 1940, **36**, 964); however, Weyl and Hauser (*Kolloid Z.*, 1951, **124**, 72), emphasizing that silicon has a marked tendency to expand its outer shell to 12 electrons by co-ordination, suggested that orthosilicic acid has the structure $H_2Si(OH)_6$, and that its polymerization is due to the aggregation of these units to form a macromolecule in which each silicon atom has a co-ordination number of 6. They represent condensation as a second stage in the polymerization.

There is little doubt that the surfaces of silica particles are normally covered by hydroxyl groups (Shapiro and Weiss, *J. Phys. Chem.*, 1953, **57**, 219). The adsorption of silicic acid on to a silica surface is, then, analogous to the first stage of the polymerization of silicic acid. We have shown, however, that dissolved silicic acid will not exchange with a silica lattice but will exchange with adsorbed silicic acid; it follows that the linkage between the silicon atoms in the surface and those of the adsorbed layer is different from the linkage between silicon atoms in the lattice. This precludes the formation of Si–O–Si linkages between the adsorbed silicic acid and the quartz surface. It is therefore improbable that this type of linking exists in the polysilicic acids, sols, and gels.

Our results, then, support Weyl and Hauser's conception that the polymerization of silicic acid is by co-ordination, but suggest that the second stage, the condensation, never occurs unless the polysilicic acid is heated, for example, under such conditions as are used for growing quartz crystals. " Gelatinous silica " and all polysilicic acids are, then, a mass of co-ordinated orthosilicic acid molecules. This view accords with many of the observed properties of polysilicic acids; indeed, on the condensation theory of polymerization, it is difficult to explain why ignited silica gel is a dehydrating agent.

Our observations neither prove nor disprove the presence of a thick disorganized layer on the surface of silica particles. They do suggest, however, that the anomalous solubility phenomena which have been reported are not due to such a layer.

EXPERIMENTAL

Reagents.—*Quartz powder.* Pure rock crystal (supplied by Hilger & Watts, Ltd.; 99·8% SiO_2) was finely powdered and a fraction containing particles of size 5—15 μ (measured microscopically) was separated by repeated sedimentation of the powder in water. A dispersion of the fraction in aqueous ethanol or sodium oxalate was set aside for some minutes and the liquid layer was transferred to the cell of a photoelectric colorimeter. A negligible galvanometer reading was produced, indicating that fine particles were virtually absent. The powder was air-dried in an oven at 120°.

Radioactive silica. Pure fused silica (" Vitreosil ") in a sealed silica tube was irradiated in the Harwell pile (B.E.P.O.) for 12 hr. The isotope of mass 30 undergoes thermal neutron capture to give the β-emitter, ^{31}Si, with a half-life of 2·85 hr.

Silicate solutions. Pure fused silica (" Vitreosil ") was fused with twice its weight of anhydrous sodium carbonate in a platinum crucible, and, after cooling, the melt was dissolved in water.

Apparatus.—The reaction vessels were 5″ lengths of 5/8″ diameter " Polythene " tubing, closed at each end by hard rubber bungs. The suspensions were continuously agitated by clipping the vessels to a horizontal rotating shaft making 60 r.p.m. The whole apparatus was immersed in a water thermostat at 25·00° ± 0·05°. The clear liquid was separated from the suspensions by centrifugation at 3000—4000 r.p.m.

Analytical Methods.—(1) *Colorimetric determination of silica.* The method used depends upon the formation and measurement of the coloured silicomolybdate complex (see King and Stantial, *Biochem. J.*, 1933, **27**, 990). The yellow colour was estimated in a single-cell colorimeter of the type described by Morris (*Brit. Med. J.*, 1944, **2**, 81), an Ilford Spectrum Violet 601 filter being used.

(2) *Isotopic assay of silica.* ^{31}Si is a fairly energetic β-emitter (1·8 Mev) and can be assayed, therefore, by liquid-counting methods. A Geiger–Muller counter described by Veall (*Brit. J. Radiol.*, 1948, **21**, **347**) was used in conjunction with a power pack and scaler ("Dynatron" Nos. 200A and 1172A).

Measurements of Surface Area.—(1) *Optical method.* A photomicrograph was made of a random sample of powder and a calibrated graticule. Enlarged prints were prepared. The mean projected area was found by cutting out the photographs of the particles, weighing them, and comparing the weights with that of standard squares based on the photograph of the graticule. The surface area was calculated by assuming that the particles were cubes.

(2) *Nitrogen adsorption.* The standard B.E.T. procedure was used. The apparatus was kindly lent by Esso European Laboratories, Abingdon.

The authors are indebted to the British Steel Castings Research Association for financial assistance.

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[*Received, October* 26*th*, 1954.]