[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies on Aging of Precipitates and Coprecipitation. XLIII. Thermal Aging of Precipitated Silica (Silica Gel)

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Although extensive investigations have been carried out on the properties (*e.g.*, specific surface, porosity and pore-size distribution, adsorptive and catalytic action) of amorphous precipitated silica (silica gel), an intimate knowledge of the structural changes that take place within the particles when the precipitate is subjected to various thermal treatments is lacking. The fact that certain structural changes must be occurring in those silica gel specimens that have been heated to high temperatures has been known for some time.[2,3] Recently Milligan and Rachford[4] have reported that sintering a silica gel causes decrease in the number of pores but no change in the average pore size. These authors have not attempted to account for the decrease in the number of pores. In a more recent paper Cohn and Kolthoff[5] have reported that on the basis of compressive strength measurements on compressed pellets of silica there exist two different mechanisms of aging,[6] a low-temperature aging occurring below *ca.* 900° and a high-temperature aging above this temperature. It is the purpose of this paper to elucidate upon the existence of these two different mechanisms of aging.

In order to discuss the mechanism of thermal aging in silica it becomes necessary first to have a "picture" of the gel particle. In the past few years the conception of the gel particle has undergone a drastic revision. Instead of a solid punctuated by a multitude of different size capillary pores and canals, Kistler, Fischer and Freeman[7] believe the structure to be "a mat or felt of filaments, needles, etc., forming a three-dimensional network." Plank[8] believes the gel to be composed of discrete particles whose diameter, from surface measurements, is of the order of 50 Å. Elkin, Shull and Roess[9] have estimated from small-angle X-ray scattering measurements the average particle size of the primary particles (assumed spherical) in freshly prepared silica gel to be around 30–60 Å. This latter view of the gel being composed of a number of primary particles is more in line with the general theory of formation of precipitates and the concept of "aging of precipitates." As will be pointed out later the thermal aging of silica gel is somewhat analogous to the thermal aging of other precipitates.[10]

Experimental

Material.—The silica gel used in these experiments has been described in greater detail in a previous publication.[11] The silica gel was a product of the Mallinckrodt Chemical Works and was labeled "Acid Silicic, precipitated, analytical reagent." A gravimetric analysis of the silica (volatility by hydrofluoric and sulfuric acids) showed 0.25% non-volatile impurities. The particle size of the gel grains varied from less than 1 μ to over 200 μ. In some of the experiments described herein it became necessary, and sometimes convenient, to use gel grains of a definite size range. The method of size separation of the gel grains with their subsequent size measurement has been given previously.[11] It is permissible to compare data obtained with different gel grain size because it has been established that varying the grain size of a particular gel does not alter the specific surface or porosity of the gel.[11]

For the sake of comparison two different lot numbers of Mallinckrodt Silicic Acid were tested, and it was found that although the absolute values of the physical properties, *i. e.*, specific surface, porosity and water content, of the original samples varied somewhat from each other (undoubtedly variations were caused by minor differences in conditions of preparation of the gel), the relative changes in the physical properties for equivalent thermal treatment were the same.

Water Content.—It is known that all of the water in silica gel is not removed completely until very high temperatures are reached.[12] That water which is removed by heating at 100° or by desiccating with phosphorus pentoxide at room temperature is referred to as "free" water while the water requiring higher temperatures for its removal is called "bound" water. The "bound" water may be retained by the solid either by being condensed in very fine pores between primary particles, or by constituting an integral part of the gel framework.[2]

The water content was determined after heating individual silica samples at different temperatures (measured by a chromel–alumel thermocouple) in an electric muffle furnace for various periods of time. The loss in weight of the heated silica after ignition at 1050° was then determined. In some cases the silica samples were weighed prior to their heating and then heated for various periods at progressively increasing temperatures with the weight of the samples being taken after each heating period. The heating period usually varied from four to seven hours and was sufficiently long to ensure practical equilibrium conditions, *i. e.*, further heating at a particular temperature for ten hours did not alter appreciably the weight of the silica. Because of the hygroscopic character of heated silica gel precautions were taken to prevent adsorption of water before and during the weighings. The water content of the silica is expressed always on the dry basis, *i. e.*, grams of water per gram of dry silica. The amount

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[1] Present address: U. S. Naval Ordnance Test Station, Pasadena, Calif.

[2] F. E. Bartell and E. G. Almy, *J. Phys. Chem.*, **36**, 475 (1932).

[3] W. A. Patrick, J. C. W. Frazer and R. I. Rush, *ibid.*, **31**, 1511 (1927).

[4] W. O. Milligan and H. H. Rachford, Jr., *J. Phys. and Colloid Chem.*, **51**, 333 (1947).

[5] G. Cohn and I. M. Kolthoff, *Festskr. J. Arvid Hedvall*, 97 (1948).

[6] The term "aging" is used in a collective sense to refer to any "structural change" that occurs within a solid.

[7] S. S. Kistler, E. A. Fischer and I. R. Freeman, THIS JOURNAL, **65**, 1909 (1943).

[8] C. J. Plank, *J. Colloid Sci.*, **2**, 413 (1947).

[9] P. B. Elkin, C. G. Shull and L. C. Roess, *Ind. Eng. Chem., Anal. Ed.*, **37**, 327 (1945).

[10] I. M. Kolthoff, *Tekniska Samfundets Handlingar*, **3**, 119 (1939).

[11] I. Shapiro and I. M. Kolthoff, *J. Phys. Colloid Chem.*, **52**, 1020 (1948).

[12] H. A. Fells and J. B. Firth, *J. Phys. Chem.*, **29**, 241 (1925).

of "bound" water present in the two lots of silica as a function of the aging temperature is given in Fig. 1.

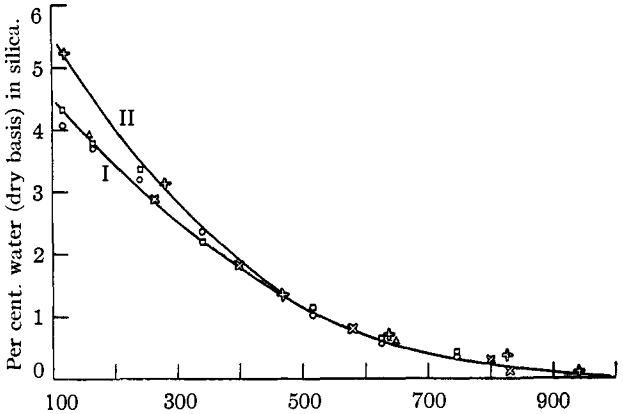

Fig. 1.—"Bound" water in silica at elevated temperatures—history of silica before thermal aging: I, silica lot no. 1—□, exposed to P_2O_5; ○, heated twenty-two hours at 115°; △, air dried, sample heated progressively; ×, air dried, individual determinations; II, silica lot no. 2—+, air dried, sized particle sample.

Surface Area Measurement.—The "free" water is adsorbed reversibly by the gel. From the amount of adsorbed water the surface area can be calculated according to the method of Brunauer, Emmett and Teller[13] using 10.6 sq. Å. as the cross-sectional area of a single water molecule,[14] or by the method of Harkins and Jura.[15]

The variation of water content with humidity was determined by the static method, *i. e.*, placing weighed samples of silica in hygrostats at 25°, reweighing the samples after equilibrium conditions had been established, and finally igniting the samples at 1050°. The relative humidity in the hygrostats was fixed by having various salts in equilibrium with their respective saturated solutions. The hygrostats were equipped with motor-driven fan blades in order to shorten the time necessary to establish equilibrium conditions.

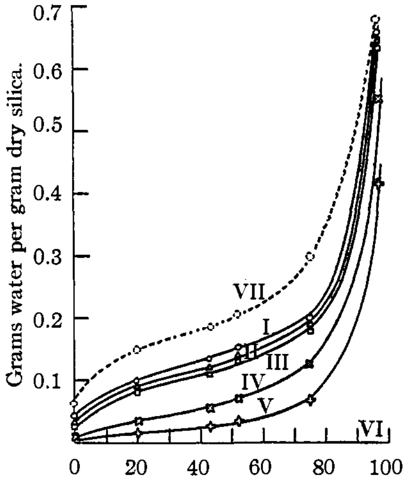

Fig. 2.—Sorption isotherms of water on silica powder at 25°: solid lines, silica lot no. 1; dotted line, silica lot no. 2. Thermal treatment: I, unheated; II, twenty-two hours at 115°; III, one hour at 265°; IV, one hour at 580°; V, one hour at 800°; VI, one and one-quarter hours at 1050°; VII, unheated.

Portions of the silica powder were "thermally aged" in an electric resistance furnace before being placed in the hygrostats. A brief description of the thermal treatment (*i. e.*, temperature and duration of heating period) of the various samples used in these experiments is given in the legend of Fig. 2 which shows the sorption isotherms of water on silica powder. The ordinate of Fig. 2 refers to "total" water, *i. e.*, "bound" water plus "free" water, per gram dry silica.

Dye Adsorption Measurements.—The use of dye adsorption for surface area measurements has certain advantages over other methods such as vapor adsorption. First, the amount of dye adsorbed is not sensitive to the temperature of the measurement, and the specific surface can be measured at room temperature. Second, a single measurement suffices to fix the surface area with a high degree of precision. Third, small changes in surface can be detected readily, and last, the surface area can be measured simply and without the need of complicated or elaborate equipment.

As a relative measure of the change in specific surface as a function of aging temperature the amount of methyl red adsorbed by various amounts of thermally aged silica powder from a 0.003 M (807 mg. dye/liter) solution of methyl red in pure, dehydrated benzene was determined photometrically. Instead of an aqueous solution of the sodium salt of the dye a non-polar solvent of the free acid dye itself was used so as to avoid any chemical interaction of the solution with the silica surface and to minimize any adsorption of the solvent which might compete with the dye molecules in occupying the surface of the silica.[16] In this connection it has been found that increasing the water content of the silica decreases the amount of methyl red adsorption. This decrease in adsorption is shown in Fig. 3 in which the amount of dye adsorption per gram of dry silica is plotted against the total water content present in the silica. Obviously the adsorbed water is effective in preventing the dye molecules from being adsorbed on the silica surface. Consequently, precautions were taken to ensure that all dye measurements on samples of silica that were thermally aged were made under conditions of no reversibly adsorbed water present in the silica samples.

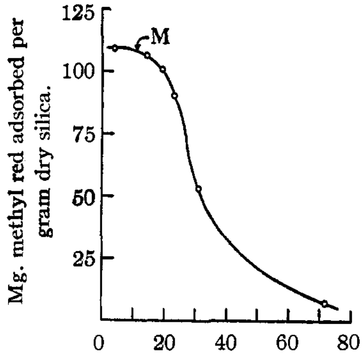

Fig. 3.—Effect of water content on adsorption of methyl red by unheated silica: M indicates monomolecular layer of water by BET method.

In previous work[10] it has been established that the specific surface of a solid is proportional to the amount of dye adsorbed only after the surface had been saturated with

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[13] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[14] H. K. Livingston, *ibid.*, **66**, 569 (1944).

[15] W. D. Harkins and G. Jura, *ibid.*, **66**, 1366 (1944).

[16] G. Grave and R. Koppen, *Z. anorg. Chem.*, **228**, 49 (1936).

the dye. For this reason the minimum equilibrium concentration of dye remaining in solution in contact with the solid when the surface of the latter was saturated was determined using the unheated silica sample and the sample after heating for seven hours at 115°. In Fig. 4 the amount of methyl red dye adsorbed per gram of dry silica is shown as a function of the equilibrium dye concentration. It is evident that at a final dye concentration of less than 0.40 mg. methyl red dye per milliliter of solution the solid silica surface is no longer saturated with dye molecules. Thus in all subsequent measurements on dye adsorption of silica samples that were thermally treated the weight of the silica samples and the volume of dye solution were adjusted such that the final equilibrium concentration always exceeded the minimum value for insuring dye saturation.

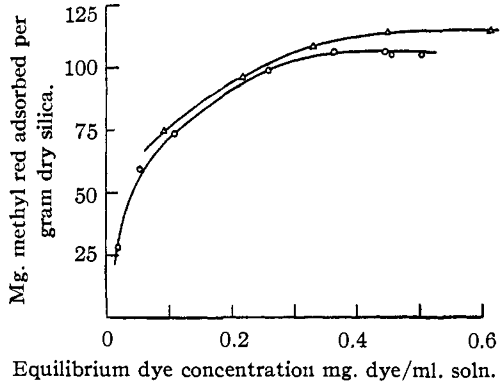

Fig. 4.—Methyl red adsorption as function of equilibrium dye concentration: ○, unheated silica, containing 14.6% water; △, silica heated seven hours at 115°, containing 5% water.

It is noted in Fig. 4 that the sample which was heated at 115° and contained no adsorbed water had a slightly higher dye adsorption than the sample of unheated silica containing 14.6% water. Apparently one-third of the water in the latter sample is present as bound water and two-thirds of the water is present in the adsorbed state. Presumably the adsorbed water accounts for the fact that the unheated sample gives slightly lower adsorptions of methyl red than the heated sample (compare with Fig. 3).

The actual procedure for the determination of the adsorption of methyl red on silica powder is comparatively simple. A given weight of silica (the weight of the silica samples usually varied from 30 to 150 mg., the higher weights being used with the samples of lower adsorptive capacity) is shaken in a glass-stoppered bottle for four to five hours at room temperature with 20 ml. of 0.003 *M* (0.807 mg./ml.) methyl red solution in benzene. After the shaking period the solid colored deep red by the adsorbed dye is separated from the solution, then a portion of the supernatant liquid (orange to yellow color) is diluted and the extinction of the dye is measured with a photoelectric colorimeter (green filter). For calibration of the colorimeter a standard solution of methyl red in benzene is diluted to various concentrations in order to get a calibration curve with low extinction values.

In the dye adsorption method the customary technique for separating the solid from the solution is to centrifuge the solution in the bottle in which the adsorption takes place. It has been found that for silica of any particular thermal treatment the amount of dye adsorption is independent of the grain size of the gel particles. This finding is in complete accord with a previous report[11] which indicated that the specific surface and porosity of a silica gel powder is independent of the gel grain size. Since the grain size is unimportant in the dye measurements, it has been found very convenient to use comparatively large grain size silica samples so that after the shaking period the silica solid would settle out of the liquid spontaneously, thereby avoiding the necessity of centrifuging the solution. The grain size of the silica powder used in the dye experiments was the same as that described under "apparent density."

It is interesting to note that the dye adsorption values for silica samples shaken for only one to two hours essentially were the same as the values obtained after considerably longer shaking periods. The comparative ease with which the dye molecules are capable of saturating the silica surface is indicative of an "open" structure of the silica gel. A discussion of this "open" structure will be considered later.

Apparent Density.—The apparent density was determined by the mercury pycnometer method. The technique for measuring the apparent density of the silica powder has been described previously.[11] In order to ensure that the mercury surrounds completely each grain, the particle size of the grains always exceeded the minimum value of 70 μ.[11] The log-geometric mean diameter of the unheated particles (silica lot 2) was 102.5 μ with a log-geometric standard deviation of 1.19.[11]

Results

Surface Area.—The sigmoidally shaped sorption isotherms of water on the thermally aged silica samples are shown in Fig. 2. The data are in good agreement with those found by Milligan and Rachford[4] in their study of the sorption–desorption hysteresis characteristics of silica gel. However, since the curves in Fig. 2 were obtained by the static method, the hysteresis effect as reported by Milligan and Rachford was not discernible. It should be pointed out that the hysteresis effect occurs only at the high relative humidities and in no way affects the calculation of the surface area from the water adsorption which is applicable only in the region of low relative humidity.

The effect of "thermal aging" of the silica powder can be recognized from the progressive change in shape and position of the curves in Fig. 2 as a function of the "aging" temperature. At comparatively low (aging) temperatures the shape of the curves is identical except for a displacement in the ordinate direction equal to the loss of "bound" water (see Fig. 1). When heated at increasingly higher temperatures the silica gradually loses its capacity to adsorb water at room temperature, and after heating at very high temperatures the silica tends to lose completely its adsorptive capacity. For example, a silica sample heated one hour at 800° still is capable of adsorbing 0.4 g. of water per gram of dry silica when exposed to a relative humidity of 97% at room temperature; however, a sample heated slightly over an hour at 1050° adsorbed only *ca.* 0.02 g. of water under identical conditions.

From the water-adsorption data the surface area of the thermally aged silica can be calculated by the BET[13] and Harkins and Jura[15] methods. However the calculations are complicated somewhat by the fact that part of the water in the silica is present as "bound" water, the exact nature of which is not clearly understood. The BET[13] equation can be written in the form

$$\frac{p}{q(p_0 - p)} = \frac{(C-1)}{Cq_m}\frac{p}{p_0} + \frac{1}{Cq_m} \qquad (1)$$

where q_m = g. vapor per g. adsorbent necessary to form a monomolecular layer, q = g. vapor per g. adsorbent at a given pressure p, p_0 = saturation pressure, and C is a constant. Once the value of q_m has been evaluated, the specific surface of the adsorbent is given by

$$S = Nq_m\sigma/M \qquad (2)$$

where S = specific surface expressed in sq. cm. per g. of adsorbent, N = Avogadro's number, σ = cross-sectional area of a single molecule expressed in sq. cm., and M = molecular weight of adsorbate. Eq. 1 is a straight line equation $y = mx + b$ in which $y = p/q(p_0 - p)$, $x = p/p_0$, $m = (C - 1)/Cq_m$, and $b = 1/Cq_m$. The value of q_m can be expressed simply by

$$q_m = 1/(b + m) \qquad (3)$$

As an example for calculating the values of q_m data[17] for silica samples heated at 300 and 450°, respectively, are plotted according to Eq. 1 in Fig. 5. From Eq. 3 the value of q_m is the reciprocal of the sum of the values for the slope and the ordinate intercept of the straight line. The values of q_m for 300 and 450° based upon the reversibly adsorbed water are 0.0775 and 0.0643 g./g., respectively. Included in Fig. 5 are data for the same temperatures but based upon the total water instead of only the adsorbed water present in the samples. It should be noted that these data also fit Eq. 1 in giving straight lines. The q_m values based upon total water amount to 0.1010 and 0.0846 g./g., respectively. The ratio of the q_m values based upon adsorbed and total water at any given temperature is approximately constant at $^3/_4$. It is difficult at the present time to say which q_m values are the more correct.

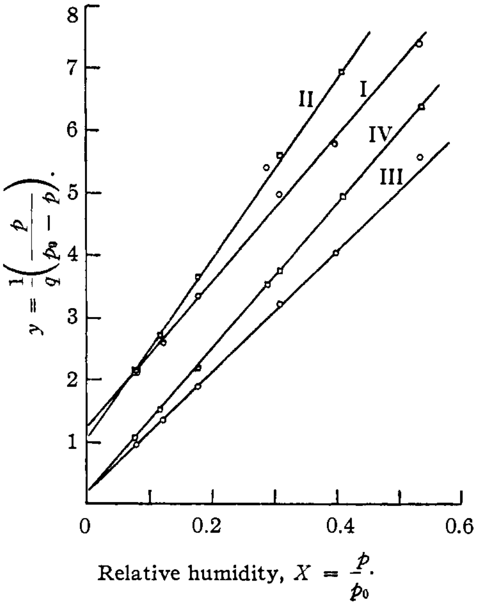

Fig. 5.—BET plots of sorption isotherms, based upon "adsorbed" water: I, 300°, b = 1.2, m = 11.7; II, 450°, b = 1.0, m = 14.6. Based upon "total" water: III, 300°, b = 0.15, m = 9.8; IV, 450°, b = 0.14, m = 11.7.

The surface area of the unheated silica (lot 2) was calculated to be 400 square meters per gram of silica based upon "total" water, and 300 square meters per gram silica based upon "adsorbed" water. While the surface area of the thermally aged silica can be calculated in the same manner, it has been found more convenient to follow the changes in surface area by the dye adsorption method.

Dye Adsorption.—The effects of water content and equilibrium dye concentration upon the amount of dye adsorption of methyl red on silica are shown in Figs. 3 and 4, respectively. With precautions as outlined previously the amounts of methyl red adsorption upon silica samples heated for various periods of time at different temperatures were determined and the relationship is shown in Fig. 6. It is noted that the general characteristics of this curve are strikingly similar to curve 24 in Milligan and Rachford's article.[4]

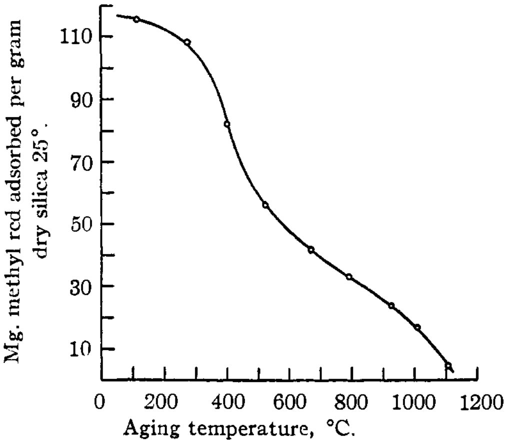

Fig. 6.—Effect of temperature upon specific surface of silica—thermal treatment: 115°, seven and one-half hours; 270°, five and three-quarter hours; 400°, four hours; 520°, three hours; 665°, five hours; 790°, six hours; 925°, one hour; 1010°, one and one-half hours; 1105°, one hour.

A comparison of dye adsorption with water-vapor adsorption measurements on unheated silica shows that 1 mg. of adsorbed methyl red dye is equivalent to 2.61 square meters of surface area if the surface area is based upon "adsorbed" water, or 3.48 sq. meters if surface area is based upon total water. From these values the effective cross-sectional area of the methyl red molecule would be *ca.* 116 sq. Å. or *ca.* 155 sq. Å., respectively. From such a large covering area per dye molecule it seems somewhat attractive to speculate that the adsorbed methyl red molecule must be flat on the

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[17] The data used in Fig. 5 have been taken from Milligan and Rachford's article[4] because of the large number of experimental measurements. Similar results can be obtained by using the data given in Fig. 2.

surface and not perpendicular to the surface. Apparently the adsorbed molecule is not held by virtue of the fact that the acid silica reacts with the NH_2 group of the dye. If this were the force responsible for the adsorption one would expect the molecule to be perpendicular to the surface.

From Fig. 3 it appears that even a monomolecular layer of adsorbed water does not hinder greatly the adsorption of the methyl red; however, water in excess of a monomolecular layer causes a pronounced decrease in dye adsorption. This sharp decrease may be the effect of a "mechanical barrier" in that the water fills the pores and prevents access of the dye molecules to the silica surface.

Apparent Density.—The data showing the change in apparent density of the silica with thermal aging are tabulated in Table I and are plotted in Fig. 7. Included in Fig. 7 are data on change of apparent density with temperature as calculated from the original data of Milligan and Rachford's work on the sorption–desorption hysteresis characteristics of silica gel. By assuming that at the saturation point, *i. e.*, relative humidity of 100%, all the water adsorbed and condensed fills completely all the void between the primary particles within the gel grain but does not represent any condensed water between grains, one calculates apparent density values which practically coincide with the experimentally measured values of the apparent density.

TABLE I

THERMAL AGING OF SILICA PARTICLES

Aging temp., t°C.	Period of heating	Apparent density (dry basis) $\rho_{t°}$ g./cc.	% Porosity	$(\rho_t - \rho_{25°})/\rho_{25°}$	$1/T \times 10^5$
25	Room temp.	0.762	65.4	~0	...
115	4 days	.761	65.4	~0	258
270	24 hours	.793	64.0	0.042	184
475	18 hours	.835	62.1	0.091	134
660	10 hours	.881	60.0	0.158	107
800	16 hours	1.045	52.5	0.372	93.2
945	17 hours	1.67	24.1	1.19	82.1
1065	1 hour	2.08	5.5	1.73	74.7
1175	4 hours	2.21	~0	1.90	69.2

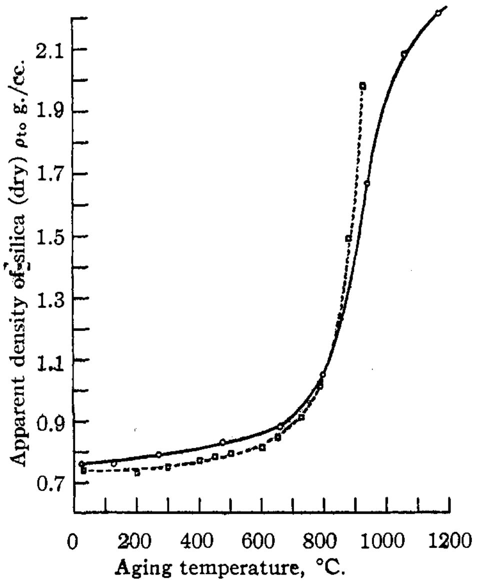

Fig. 7.—Effect of thermal aging upon apparent density of porous silica powder: ○, experimental data; □, calculated from Milligan and Rachford's water sorption data.

Discussion

From the foregoing results on the variations in physical properties, *i. e.*, surface area and porosity, of silica gel with thermal aging, it appears that the use of surface area measurements calculated either from water adsorption or from dye adsorption data as a criterion for following the degree of thermal aging in silica may be subject to criticism. The lack of knowledge of the exact nature of the "bound" water in silica makes surface area calculations by water adsorption data uncertain, and likewise the size of the dye molecules compared with the size of the pores may render the dye adsorption data invalid. On the other hand, data based on apparent density measurements appear to be reliable since the values can be measured directly and are independent of the internal structure.

Aging manifests itself in a perfection process of the arrangement of the building stones, *i. e.*, ions, atoms or molecules, of a material. This perfection can take place through a diffusion process of the building stones which move from thermodynamically unstable positions to positions of lower thermodynamic potential. Starting with a porous structure the perfection of the crystallites will result in an increase in apparent density (or decrease in porosity) to some maximum value corresponding to the true density of the solid.

From the abrupt change in the slope of the curves in Fig. 7 it is evident that there exist two different mechanisms of aging, a low temperature aging occurring below *ca.* 700° and a high-temperature aging above this temperature. It is interesting to note that this critical temperature which is 0.5 of the melting point on an absolute temperature scale corresponds to Tammann's "relaxation temperature,"[18] *i. e.*, the temperature at which incipient recrystallization of the bulk of the material becomes detectable.

In all simple diffusion or conductivity processes one would expect the migration of building stones, *i. e.*, ions, atoms or molecules, as a function of temperature to follow the well-known exponential law, *viz.*

$$D = Ke^{-E/kT} \qquad (4)$$

where D is the diffusion constant, E is the energy of activation, T is the absolute temperature and

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[18] G. Tammann and A. Sworykin, *Z. anorg. Chem.*, **176**, 46 (1928).

K,*k* are constants. In practice it is not necessary to measure actually the diffusion constant itself but one can follow some process which is directly related with the diffusion constant. Previously[5] it was believed that both the increase in strength of compressed pellets and the decrease in thickness of the pellets as a function of temperature were related directly with the diffusion of the building stones of the structure; however plots of logarithm of strength and thickness of the pellets *vs.* reciprocal of absolute temperature yield slopes which differ considerably from each other. Since diffusion in aging processes takes place by the irreversible migration of certain building stones from thermodynamically unstable positions to positions of lower thermodynamic potential, it is possible that the relative change in apparent density from that at room temperature would be more closely related to the diffusion constant than the absolute value of the apparent density or of the length of the pellet. In Fig. 8 are plotted the logarithms of the relative change in apparent density $(\rho_{t^\circ} - \rho_{25^\circ})/\rho_{25^\circ}$ of the silica grains *vs.* the reciprocal of the absolute temperature with the resultant sharp break in the curve. The pronounced change in slope of the curve evidently is characteristic of a change in diffusion mechanism from a "surface diffusion" to a "bulk diffusion."[19] It is of interest to note that the break is found at a temperature of 700°. Before any calculation of the activation energies from the slope of the curves in Fig. 8 can be made, it will be necessary to establish more fully the proportionality between diffusion constant and the experimentally measured values of the relative change of the apparent density.

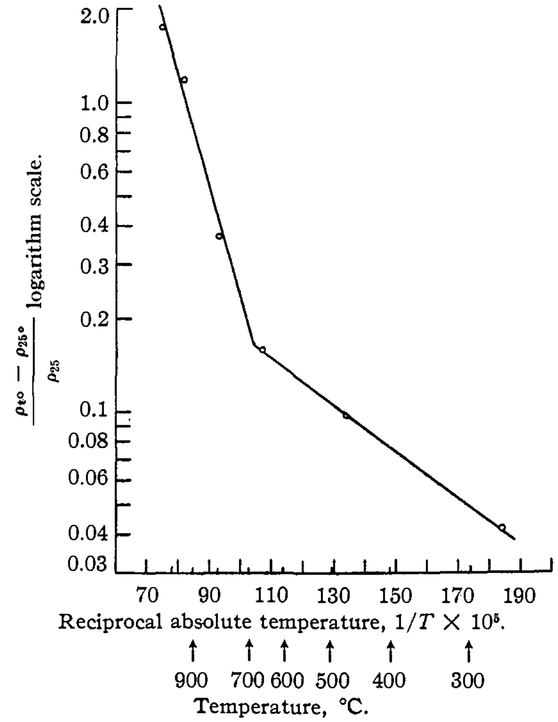

Fig. 8.—Plot of log $(\rho_{t^\circ} - \rho_{25^\circ})/\rho_{25^\circ}$ *vs.* $1/T$.

A comparison of the porosity (Table I) of the silica grains which were heated to various temperatures with their corresponding surface development (Fig. 6) leads to some unexpected results (Fig. 9). If the silica grains actually are composed of discrete (primary) particles, then the high porosity indicates that these primary particles are not in contact, or have exceedingly few points of contact, with each other. After heating the silica grains to some temperature, say 700° or less, the porosity decreases slightly yet the surface area decreases considerably for the same temperature range. This anomalous change in surface area with porosity cannot be attributed to the inaccessibility of dye molecules or water vapor molecules to the internal surface of the grains since pycnometer studies using benzene as the pycnometer liquid show the same "true" density of silica within the temperature range under consideration.

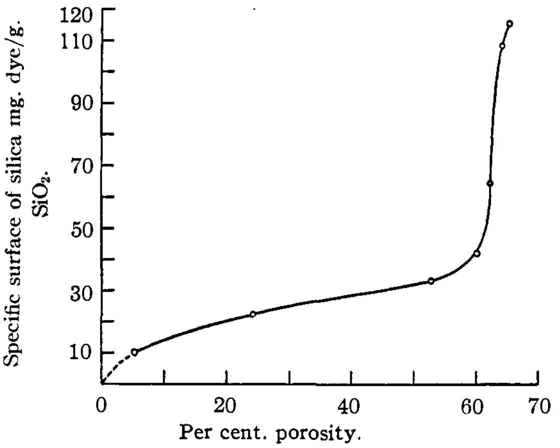

Fig. 9.—Change in specific surface of silica as function of particle porosity.

The anomalous change in surface area with porosity may be explained in the following way. The primary particles though spherical in shape nevertheless have a very irregular surface contour, and therefore may have an extremely large active surface. At room temperature the gel grain is composed of a very loose network of primary particles which have only few points of contact with each other. As the aging temperature increases but does not exceed the critical temperature (*ca.* 700°), a marked "perfection" of the individual primary particles *via* surface diffusion occurs with a corresponding decrease of the surface. The mobility of the surface silica molecules is enhanced by the presence of water vapor which facilitates breaking of –O–Si–O–Si–O– bonds to form –O–Si–OH HO–Si–O– bonds.[5] This low temperature aging results in a marked decrease in internal surface but in a very small decrease in porosity. At temperatures above the critical temperature the

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[19] I. Shapiro and I. M. Kolthoff, *J. Chem. Phys.*, **15**, **41** (1947).

bulk diffusion of the silica molecules produces sintering of the primary particles with a resultant sharp decrease in porosity as well as a decrease in surface area. This "cementing together" of primary particles at elevated temperatures increases the strength of the gel grains and its resistance to compaction under pressure.[20]

The above described mechanism of thermal aging of silica gel suggests an "open structure" arrangement as compared to the conception of "cylindrical pores" which still is being advocated in the literature. The comparatively rapid rate of penetration of dye molecules into the gel grain would tend to favor the former type of structure. Also, the authors would like to point out that the results reported here appear to be contradictory to the conclusions reached by Milligan and Rachford that sintering a silica gel causes destruction in the number of pores but no change in the average pore size.[4] In the light of the numerous investigations on "aging of precipitates" carried out in this Laboratory it is difficult to conceive how a porous structure like silica gel can collapse on heating without being accompanied by a decrease in "average pore size." Since the experimental data reported here are in agreement with the data given by Milligan and Rachford, it is felt that the discrepancy is due to the use and interpretation of the Kelvin equation in calculating the "average pore size."

One of the common methods of arriving at a figure for the diameter of the primary particles is to calculate the diameter from surface area measurements. For example for silica (true density = 2.20 g./cc.) with a specific surface of 300–400 sq. meter/g. silica the calculated diameter of the primary particles (assumed to be spherical) would be *ca.* 70–90 Å. According to the mechanism of aging as set forth in this article the average diameter of the primary particles will be somewhat greater than the value calculated from surface area measurements due to the fact that surface irregularities as well as the smallness of the particle size contribute to the large surface development of the silica gel.

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Summary

The thermal aging of precipitated silica (silica gel) has been studied by determining the changes in specific surface by water adsorption and dye adsorption measurements and by determining the change in apparent density by the mercury pycnometer method as a function of temperature.

Unheated silica gel is believed to consist of a very loose network of minute primary particles, perhaps roughly spherical in shape, but with an irregular surface contour. Upon heating the gel to temperatures below *ca.* 700° the individual primary particles undergo a "perfection" process *via* a surface diffusion of the silica molecules from thermodynamically unstable positions to more stable positions. This perfection results in a decrease in surface area but with very little decrease in porosity. At temperatures above 700° the bulk diffusion of the silica molecules results in a sintering of the primary particles as indicated by a pronounced decrease in porosity and a corresponding decrease in surface area.

The use of surface area measurements for calculating the average particle diameter in porous gels tends to give values which are smaller than the actual diameter.

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[20] I. Shapiro and I. M. Kolthoff, to be published.

[CONTRIBUTION FROM THE UNIVERSITY OF UTAH]

The Constitution of Chromic Salts in Aqueous Solution[1]

BY H. TRACY HALL[2] AND HENRY EYRING

It has been known for a long time that aqueous solutions of chromic sulfate exist in both a violet and a green form[3] but the isolation of any definite compounds from the green solution has not been successful. The green solutions of chromic sulfate are obtained either by heating or aging violet solutions. The violet solutions are obtained directly by dissolving violet crystals of chromic sulfate or chrom alum.

It was early recognized that the acidity of the boiled or aged solution of chromic sulfate was greater than that of a violet solution of corresponding concentration. Recoura[4] determined the heat exchanges accompanying the addition of different amounts of sodium hydroxide to given amounts of green chromic sulfate solution (prepared by boiling a violet solution). When the heat liberated was exactly the same as that liberated during the addition of the same amount of sodium hydroxide to an amount of sulfuric acid

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[1] Presented before the Physical and Inorganic Division of the American Chemical Society at the 112th National meeting in New York City (Sept. 1947). The work reported in this paper is taken in part from the doctoral thesis submitted by H. Tracy Hall to the faculty of the University of Utah in partial fulfillment of requirements for the degree of Doctor of Philosophy.

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[3] See, for example, the chronological bibliography of the change from violet to green in chromic sulfate from 1841 to 1912 given by Graham, *Am. Chem. J.*, **48**, 187–190 (1912).

[4] Recoura, *Ann. chim. phys.*, [7] **4**, 494 (1895).