SILICA GEL

A Thesis

Submitted to the Faculty

of

Michigan State College

In Partial Fulfillment of the

Requirements for the Degree

of

Doctor of Philosophy

Department of Chemistry

By

Benjamin Levi Smits

1926

ACKNOWLEDGMENT

I wish at this time to express my appreciation of the help and kindly suggestion given to me by Doctor D. T. Ewing during the progress of this work.

THE FACTORS INFLUENCING THE ACTIVITY OF SILICA

There are many factors which tend to effect the porosity of silica gel, which may be modified by the method of preparation. The object of this investigation has been to determine a few of these factors with the idea of developing a method of preparation that would avoid as many of the defects of the other methods as possible.

The two methods in general use today are namely,-- the method developed by Patrick,[1] which consists essentially of decomposing sodium silicate by means of hydrochloric acid and washing the fresh undried gel free of its acids and chlorides and then drying it; and the method originally reported by Briggs[2] in 1921 of allowing the unwashed gel to dry to a rigid solid at 390° C. and then washing it in boiling water. The high temperatures used by Briggs[2] and later by Fells and Firth[3] have been found to be unnecessary for the production of an active gel.

Holmes,[4] investigating methods to improve the mode of washing the acids and salts from silica gel, found that a gel dried to a rigid solid at temperatures little above that of the average laboratory gave an exceptionally active gel. He holds that this is partly due, at least, to the support given the gel structure by the chloride solution. The criticism of the Patrick[1] method is that the capillaries of the soft fresh gel are especially liable to collapse and injury during handling and washing.

The gels of colloidal silicic acid, or the so-called soluble silica, obtained either by the decomposition of an alkaline silicate in the presence of an excess of the acid or by the hydrolysis of a silicon

compound have been the object of study of many chemists. The history of this research has been given by Fruhling[5] in 1895 and later continued by Walden[6] in 1910. As early as 1773 Baume'[7] demonstrated the existence of what he called a soluble form of silica obtained when a solution of liquor silicium was treated with an excess of acid.

The use of diatomaceous earth or Kieselghur[8] as a decolorizing agent is of great antiquity. This substance is found in marine deposits in many places, being made up of the siliceous skeletons of diatoms, the silica probably in a colloidal form having been derived from the water in which the diatoms lived. A good quality of Kieselghur should absorb at least four or five times its weight of water. It was because of this liquid holding capacity of diatomaceous earth that Nobel[9] decided upon its use as a vehicle for nitroglycerine in dynamite since it will hold as much as 75% nitroglycerine and still remain dry enough to mould into sticks.

In 1830 Berzelius[10] prepared gels of silicic acid by two different methods. In one he treated silicon tetra fluoride with water which upon evaporation set to a gel and in the other he treated crystallized boric acid with silicon fluoride, removing the fluorides and borates by the use of a large excess of ammonia. In 1846 Ebelman[11] hydrolyzed ethyl ortho silicate forming a gel. Although these early workers only vaguely guessed the colloidal nature of soluble silica their contributions to the knowledge of its chemical properties are invaluable.

Various methods have been developed of preparing the hydrogel of silica by means of electrolyzing a solution of an alkaline silicate. Becqueral[12] recorded the formation of gelatinous silica about the positive pole when an electric current was passed through a solution of potassium silicate. Kröger,[13] working with a cell in which the anode

was separated from the cathode by means of a porous cylinder, found that with a 1.5% solution of sodium silicate a clear hydro sol of silicic acid was formed in the anode chamber, which did not gel within four weeks, electrolyzing a 6% solution gave a hydro sol which set almost instantaneously, while with a 30% solution a dense gelatinous form of silica was deposited on the anode. Spencer and Proud[14] prepared what they termed ortho silicic acid by electrolyzing a 50% solution of water glass using a very heavy anode current density.

The history of silica gel however properly dates from the work of Thomas Graham[15] in 1861. He was the first to show that the clear limpid solution obtained by the decomposition in the presence of an excess of acid of an alkaline silicate solution by an acid according to the following idealized reaction:

$$Na_2SiO_3 + 2\ HCl = H_2SiO_3 + 2\ NaCl$$

(since water glass is not such a simple compound but a complex mixture) would not diffuse through the pores of an animal nor a vegetable membrane.

A hydrosol of silicic acid used by Graham[15] in his work was obtained by mixing with constant stirring equal volumes of a ten per cent solution of sodium silicate and also a ten per cent solution of hydrochloric acid. This colloidal solution was freed from its admixture of chlorides and acid by dialysis. Graham's[15] hoop dialyser consisted of a glass cylinder open at both ends and so arranged that a piece of animal or vegetable membrane could be stretched across one of the open ends and held in place by means of a metallic hoop. The solution to be dialyzed was placed on the cylinder and the apparatus suspended in such a way that the membrane was in contact with the surface of water. Graham[16]

found that after dialyzing for four days, the water being changed occasionally as the electrolytes diffused into it, the solution in the dialyzer was not rendered turbid by the addition of reagent silver nitrate. The dialyzed hydrolsol of silicic acid fails to show the usual Tyndall[17] cone observed when a beam of light is focused, in a colloidal solution indicating that at least in this condition the molecular aggregations are not sufficiently large to scatter light.

Although the majority of chemists have used hydrochloric acid to effect the decomposition of the alkaline silicates in the preparation of silica gel, the use of many other acids has been reported. Plessy[18] in 1855 using acetic acid prepared a very interesting gel which he termed artificial hydrophane. Monier[19] reports the use of oxalic acid, while Meunier[20] found that sulphuric acid decomposed sodium silicate to form a firm translucent gel. Holmes[21] has prepared a useful table in which he gives the concentration of a number of acids both organic and inorganic, which, when mixed with equal volumes of sodium silicate solution of a certain density and $Na_2O : SiO_2$ ratio, results in a gel which will set in any desired time. Holmes'[22] studies of the relationship existing between syneresis and vibrations of gels are of interest.

Of the three common inorganic acids -- hydrochloric, nitric, and sulphuric -- hydrochloric reacting with sodium silicate gives a gel which can be purified of its alkaline salt and excess acid while the use of nitric acid results in a gel which it is almost impossible to free from the nitrate ion. The gel formed by sulphuric acid stands midway between the two extremes according to Gmelin-Kraut.[23]

There are many factors which influence the rate of setting of silica gel. Graham[16] found that the addition of powdered graphite caused a dialyzed sol to set to a gel within two hours while carbon dioxide caused it to become turbid. Fleming[24] working on the rate of setting stated that the hydrogen and hydroxyl ions have a catalytic effect upon the coagulation of the gel. He has summarized his findings by saying that as the concentration of the hydrogen ion increases the rate of setting is at first retarded and then accelerated, while in the case of the hydroxyl ion concentration the rate of setting is at first accelerated with increasing concentration and then retarded. Holmes[21] found that the dehydrating influence of the unionized acid molecule had a greater effect than either the hydrogen or hydroxyl ion concentration.

Graham[15] found that he was able to obtain a chlorine free sol of silicic acid by four days of dialysis while in the work of Jordis[25] it took nearly three weeks to remove all traces of chlorine and from four to six weeks before the sodium had disappeared. Zsigmondy and Heyer[26] working with an improved form of dialyses confirmed Graham's[15] original findings. However, as a means of producing a satisfactory silicic gel in quantities sufficient for an extended research problem, dialysis is much too slow.

It has been demonstrated that an active gel can be produced by allowing the colloidal sol of silicic acid to set to a solid gel while still containing the sodium chloride formed as a by-product of the reaction between sodium silicate and hydrochloric acid along with the excess acid and later washing the gel free of these electrolytes. The effect of the hydrochloric acid and sodium chloride upon the porosity of the gel is probably that of increasing the size of capillaries.

Wumder and Suleiman[27] have shown that at ordinary temperatures gelatinous silica is soluble to an appreciable extent in dilute hydrochloric acid. J. von Bemmelen[28] found that the dried gel adsorbed hydrochloric acid from dilute solutions and is of the opinion that the acid replaces the water of structure of the gel. Jordis[29] has pointed out that the early observation on the solubility of gelatinous silica, such as that of Graham[16] who found that 100 grams of water at ordinary temperatures dissolved 0.021 grams of silica, did not take into effect the influence of traces of acid and also of the alkalies derived from the glass utensils.

Jordis[29] has shown that when firm gelatinous silica gel still containing the by-products of the reactions between sodium silicate and hydrochloric acid is washed in cold water, the wash waters soon become free of both Cl^- or Na^+ ions. However if this same gel is again digested using water at the temperature of 100° C., it was found that the wash waters show strong evidences of chlorine and sodium. If the digestion is continued at this temperature, the amount of alkaline salt in the water does not decrease but reaches a minimum value and continues there in spite of the duration of the digestion. Jordis and Karnsten[30] are of the opinion that some compound is formed between the hydrochloric acid and the silica, as are also Mylius and Groschuff.[31] Water freed of all alkalies and acids has been shown by Lenher and Merrill[32] to act as a solvent upon the dry gel, solubility depending directly upon fineness of grinding, temperature, and pressure. The water first converts the powdered silica into a gel and later dissolves it. Mellor[33] has shown that sodium chloride in solution acts to increase the solubility of gelatinous silica.

Silicic acid at ordinary temperatures is one of the most feeble

inorganic acids known and it is probable that if it was isolated it would very readily dissociate into silica and water. However the large number of naturally occuring silicates gives evidence of its existence. Many of the earlier chemists have recorded their efforts to determine whether there existed a definite hydrate of silica. Ebelman[11] obtained a gel by the action of moist air upon silicic ether which when air dried appeared as a glassy, amorphous substance which had the composition of $2SiO_2\ 3H_2O$. Fremy[34] found that if the same gel was dried in vacuo that the molecular composition was $3SiO_2\ 2H_2O$. Doveri[35] prepared a gel by decomposing an alkaline silicate with hydrochloric acid which when dried in vacuo over concentrated sulphuric acid corresponded to Ebelman's[11] hydrate. Fuchs[36] obtained two hydrates of silica, one with a composition of $3SiO_2\ H_2O$ and the other $4SiO_2\ H_2O$. Graham[16] and also Roberts[37] found that if the clear transparent gel obtained by allowing a dialyzed sol of silicic acid to gelatinize and drying the gel so obtained in vacuo at 15^0 C. was further dried over concentrated sulphuric acid, it corresponded to the formula of meta-silicic acid $SiO_2\ H_2O$.

J. von Bemmelen[38] has made an exhaustive study of the physical properties of the hydro gel of silicic acid. In an investigation of the equilibrium conditions existing between the dehydrated gel and the water vapor in which it was in contact, he found that the dehydration curve was not reversible, but that rehydration takes a shorter course to reach the saturation curve representing the vapor pressure of water at that particular temperature. He also found that the nature of the rehydration curve varied with the age and method of preparing the gel. According to von Bemmelen,[38] the hydrogel of silicic acid is of an unstable composition

of the general composition SiO_2nH_2O in which the value of n is determined by the previous history of the gel. Jordis[39] concludes from von Bemmelen's[38] work that the amount of water in a gel at equilibrium is proportional to the partial pressure of the water in the surrounding atmosphere. Zsigmondy[40] explained the hysteresis on the dehydration curve on the assumption that after the primary dehydration there is a film of adsorbed air on the surface of the capillaries which the water can not wet.

Carnelley and Walker[41] working with inorganic oxides found in dehydrating a sample of pure silica obtained by the decomposition of an alkaline silicate by means of hydrochloric acid that there was a terrace on the dehydration or time-temperature curve just below 100° C. There was not however a sufficiently abrupt change in the rate at which the water vapor was given off to account for the existence of any definite hydrate. J. von Bemmelen[38] later showed that this terrace on the dehydration curve was characteristic of other colloidal gels.

Mellor[42] has summarized this extensive work on the hydrates of silicic acid by stating that the majority of these hydrates are but arbitrarily selected states in a continuous series between the sol of silicic acid and dehydrated silica and are represented by arbitrarily selected points on a continuous drying curve. In this connection it is interesting to note that Faber and Olsen[43] working at the Edgewood Arsenal research laboratory, Maryland, U.S.A., found that silica gel could be used repeatedly without loss of efficiency for the adsorption of many different vapors, such as water, benzene, nitrous oxide, and nitric acid, provided that the temperature of reactivation did not exceed 250° C.

The history of the influence of physical factors upon the gels of silicic acid is not complete without some reference to the work of Tschermak[44]. Tschermak[44] has proposed a system of classifying the different silicic acids based on the natural silicate from which these are obtained by decomposition with hydrochloric acid. He has shown that these various gels showed a lag in their dehydration at different temperatures and assumed that it was due to a change from the evaporation of absorbed water to a dehydration of the loss of water of structure and represented a definite acid. Mügge[45] has shown that the rate of dehydration observed by Tschermak[44] depended upon the temperature of dehydration and that the hysteresis in the dehydration curve could not be interpreted as a transition from absorbed water to a loss of water of structure. It has been further shown that the A. Suida[46] reaction of methylene blue towards Tschermak's[44] acids was due to the changes in the hydrogel brought about by the gradual loss of water.

Graham[16] found that it required a very small quantity of alkali to neutralize a dialyzed sol of silicic acid and concluded from this that it must have a very large molecular weight. Sabeneff[47] from boiling point and freezing point determinations on the sol of silicic acid calculated that the value of n in the formula $(SiO_2)_n$ must lie somewhere between 800 and 1000 or that the molecular weight was over 40,000. Since the colloidal sol of silicic acid is not a homogeneous solution but a homogeneous suspension, the laws of osmotic pressure applying to dilute solutions can not be applied in the case of silicic acid.

The specific gravity of the hydrogel as determined by different workers has been found to vary from 1.50 and 2.390. These values are of

little worth however since it has been impossible to determine the state of matter in which the water is that is held on the surface of the capillaries. Anderson[48] found that the specific gravity of the gel thoroughly permeated with water was 1.5, that of the dry gel was 1.980, and that of the gel substance was 2.048. Berl and Urban[49] found that a gel dried at 25° C. had a specific gravity of 2.465, dried at 300° C. 2.390, while when dried at 1000° C. the specific gravity had fallen to 2.271. When the gel was further digested in concentrated hydrochloric acid and after evaporation ignited to a white heat, the dehydrated silica had a specific gravity of 2.627. Ruth[50] found that a gel in which the adsorbed water had been replaced by ammonia and evacuated at a temperature of 250° C. had a specific gravity of 2.210.

Physically the gel of silicic acid is apparently made up of a cellular or net-like structure penetrated by innumerable capillaries. J. von Bemmelen[38] has studied this structure microscopically and applied the term "wabenstruktur" to the condition that he found. He stated that this structure was due to two solutions of markedly different concentrations, the more concentrated forming the walls of a mass of cells which enclosed the more dilute solution. Bütschli[51] found that this net-like structure appeared at certain stages in dehydration of the gel and later disappeared. The foam-like structure mentioned by Bütschli[51] has been shown to be due to refraction phenomenon. The gels prepared by Butschli[51] and also by von Bemmelen[38] appeared at a certain stage in dehydration to be opaque and as the dehydration progressed further to become clear. Biltz and Geibel[52] were among the first to study the physical structure of the gel by means of the ultra microscope. The observations of Zsig-

mondy[53] upon the physical structure of the gel agreed with those of the earlier workers concerning the macro structure, but he has shown from his ultra microscopic investigations the pores of a gel dried slowly into a compact mass were amicroscopic in size ranging from 3.65 uu to 5 uu. The coarse structure observed by Bütschli[51] was shown to be due to an accumulation of water in the larger extra cellular spaces. Zsigmondy[53] found that by saturating a gel with benzene the true ultra microscopic structure was revealed, since the index of refraction of the benzene corresponded so closely with that of the gel structure.

Anderson[48] studying the problem of pore size from the angle of the lowering of vapor pressure due to the presence of a large number of extremely fine capillaries obtained values which agreed with those of Zsigmondy.[53] Bachman,[54] observing the process of gelatinization of a hydro sol of silicic acid ultra microscopically, found that the amplitude of the Brownian movement decreased coincident with an increase in the size of the molecular aggregations due to gel formation. During the process of aging, the cellular structure of the gel becomes less distinct and appears finally as an ultra microscopically homogeneous system.

According to von Weimarn[55] a gel is formed when the degree of momentary super saturation of the precipitate is excessively high, the degree of dispersion being a direct function of this super saturation. Pappada and Sadowski[56] have distinguished between coagulation and gelatinization, arguing that since in gelatinization there is a smaller concentration of the silicic acid consequently there is more time allowed for the orientation of these extremely fine granules. La Chatelier[57] holds that at no

time is the silica in a dissolved state, but that it is held in a gel structure by the extreme hydration of the particles. J. von Bemmelen[58] states that the water holding capacity of the dehydrated silica gel is decreased by its formation from a concentrated solution of silicic acid in which rapid coagulation takes place, by rapid prolonged drying and, under adverse conditions, by age.

This extensive review of the literature relating to silica gel has not been made with the idea of covering the entire field, but has been done with the idea of bringing out if possible those facts which have been shown to have a direct effect on the physical properties of the final dehydrated product. Credit should be given to the excellent bibliographies found in Mellor's[59] Comprehensive Treatise on Inorganic and Physical Chemistry and also in Gmelin-Kraut's[60] Handbuch der anorganische Chemie.

The term silica gel is of course a misnomer, as it is now generally applied to the hard, glass-like substance derived by dehydrating the gelatinous precipitate of silicic acid. The factors influencing the adsorptive activity of this form of silicic acid can be grouped into three general classes.

1. Mode of preparation.

2. Mode of freeing the hydrosol of the by-products of the decomposition of an alkaline silicate or the by-products of hydrolysis.

3. Mode of drying which also includes the temperature of final activication.

J. von Bemmelen,[38] Holmes,[4] and others have shown that the most active gel results from a hydrosol sufficiently dilute of silicic acid which requires an appreciable time to gelatinize after mixing the

acid and silicate solutions together, in order that in the orientation of the molecules of silicic acid there can be an orderly aggreation into colloidal particles.

As a means of preparing a quantity of silica gel necessary for any extended research, hydrolysis of a silican compound may be dismissed due to the difficulties encountered. Hydrolysis as a mode of preparation has however a real value, since by the use of a compound such as silicon tetra fluoride, hydrofluric acid, the by-product of the reaction,

$$SiF_4 + 4H_2O = H_2SiO_3 + 4HF + H_2O$$

is volatile and can be easily removed from the resulting hydrosol and a very pure gel can be secured.

The method used in preparing any quantity of silica gel is however in general practice the decomposition of an alkaline silicate, usually water glass, by means of an acid. As has been shown, the gel resulting from the use of hydrochloric acid for this purpose can be more readily freed of the electrolytes than the gels made from other mineral acids.

There are two general methods used for freeing the hydrosol of silicic acid of its electrolytes. One consists of dialyzing the acid sol of colloidal silica until the electrolytes have all been removed by diffusion and subsequent gelatinization of the pure sol. This method results in an extremely compact, fine-pored gel, but is difficult when applied to quantity production. The other method is that in general use by the majority of workers at the present time. It consists of allowing the acid hydrosol of silicic acid to gelatinize and then washing it free of its acid and sodium chloride.

still
U. S.
the g
of the
hand,
concer
reache
tially
sults.
time i

form c
of the
uble c
by was

having
1 & 3,
to be
tainin
been

If the hydrogel is washed free of its electrolytes while it is still in a soft jelly-like condition, as described in Patrick's[1] first U. S. Patent, there is a great possibility of injuring the activity of the gel due to partial collapse of the capillary spaces and obstruction of the ultra microscopic pores of the external surface. On the other hand, if such a gel in its original condition is allowed to dry until the concentration of the sodium chloride solution in the capillary spaces reaches the point where crystals are deposited, these spaces are evidentially injured, possibly by the splitting force, and an inactive gel results. As will be shown, there is a definite degree of drying at which time if washing is instigated an exceptionally active gel results.

Probably the most important single factor in producing an active form of silica gel is the method of drying, and this effect is independent of the condition of the gel; that is, whether it still contains its soluble chlorides and hydrochloric acid or whether these have been removed by washing. Rapid drying invariably results in an inactive gel.

EXPERIMENTAL

The water glass used in this work was a water-white product having an original density of 1.4042 with a ratio of Na_2O to SiO_2 of 1 : 3.46. There was a trace of iron present, but it was not considered to be large enough to materially affect the results. Water glass containing approximately the same distribution ratio of Na_2O and SiO_2 has been found by Holmes to give the most satisfactory results.

TABLE I

Composition of Water Glass

Silica (SiO_2)	27.50%
Sodium oxide (Na_2O)	7.49%
Moisture	57.22%
Specific gravity	1.4042

The water glass was diluted to a density of 1.18 by adding it with agitation by means of compressed air to the water, rather than by adding the water to the silicate, the resulting diluted solution being colorless and free from traces of coagulated particles. As the same apparatus was used in diluting the water glass solutions as was used in mixing the silicate with the acid solution, it will be described here. A large mouthed bottle having a capacity of at least twice the volume of gel solution desired, so as to avoid loss due to the excessive foaming, was fitted with a stopper through which a funnel and four glass tubes were passed. These tubes were long enough to reach nearly to the bottom of the bottle and had their lower ends bent in such a way so as to produce a whirling effect in the solution when compressed air was forced through them. A vent large enough to allow of the free escape of the air should be provided in order that there may be no back pressure on the funnel through which the water glass is added. The funnel should be so orientated that the falling silicate solution does not strike the compressed air tubes. By using this method for diluting the water glass solutions the ill effects due to the presence of dissolved carbon dioxide in the water are eliminated, since in this way the water is considred to be a

potential acid due to the CO_2. The density of the diluted water glass, 1.18, was determined experimentally as being nearly as high as could be used with an equal volume of 3.8 hydrochloric acid to give uniformly good results.

The method of preparing the gels used in these preliminary investigations was as follows. The colloidal solution of silica obtained by mixing equal volumes of water glass and hydrochloric acid, as previously described, was poured into shallow crystallizing dishes and allowed to stand until the gel was firm enough to handle. Large variations in temperature were avoided, the average being 18.5° C. As soon as the gel had reached this condition of firmness, it was removed from the dishes, and after being broken into inch cubes was placed upon cheese cloth racks in a drying room with an average temperature of 45° C. Drying was continued until the smaller pieces of gel showed a tendency to split due to the formation of sodium chloride crystals in the capillary spaces. The larger lumps of gel at this stage of dryness were rigid pieces with a glassy surface when broken, having a water content of between 55% and 65%.

The gel in this condition was then washed by decantation until the wash water did not show a trace of opalescence due to chlorides when tested with reagent silver nitrate solution. After washing the gel was further dried at the same temperature, 45° C., until it had reached the point where there was no further change in volume of the gel pieces due to dehydration. The water content of an active gel in this condition was found to be 14%. Final activation of the gel was obtained by placing it in a U-tube submerged in an oil bath and drawing a slow stream of pre-

heated air through it free from the usual laboratory fumes and dried by means of $CaCl_2$. The temperature of the oil bath was gradually raised from 40° to 225° C., the time required for securing this temperature being never less than two hours. Activation was continued after this temperature was reached, the time depending upon the amount of gel, until the water content had fallen to between 6 and 7%. The gel in this active condition was protected from fumes by being kept in glass stoppered bottles.

The adsorptive capacities of the various gels used in this work were determined dynamically. Air saturated with benzene vapors was passed over a weighed sample of the gel and the sample weighed again when it had reached saturation. Benzene was selected because of its relatively low boiling point.

The adsorption train used for this purpose was set up as follows. Air drawn from out-of-doors by means of a suction-blower was dried by passing through a calcium chloride tower. As the rotar of the suction-blower moved in oil it was necessary to provide a trap for oil vapor which consisted simply of a flask submerged in a freezing mixture.

As a final precaution against the possibility of any oil particles being carried over by the air stream, it was passed through a tube lightly packed with cotton wool and then through a calcium chloride drying tower. The rate of flow was determined by passing the air through a flowmeter. This was provided with a trap to catch the mercury with which the flowmeter was filled in case of an accident to the blower. The rate of flow of air used throughout the work was an average of thirty cubic centimeters of air per gram of gel.

The metered air was saturated with benzene vapors by being

passed through saturators so constructed that there was the minimum of contact between the benzene-saturated air and the rubber connections. The saturators were completely submerged in a constant temperature water bath maintained at 12.5° ± 1° C. After leaving the saturators, the air passed through a spray catcher filled with glass wool and into the gel tube.

The gel tube consisted of a glass U-tube, with short side arms, fitted with perforated ground glass stoppers. The U-tubes used held approximately ten grams of gel. In order to avoid the possibility of there occurring a condensation of the benzene vapors in the gel tube, it was maintained in a water bath at a constant temperature of 25° ± 0.5° C.

A number of preliminary runs were made with this apparatus to determine its stability. With an air stream (320 cc. per minute) saturated with benzene vapors at 12.5° C., a sample of silica gel obtained from the Silica Gel Corporation showed a capacity to adsorb 27.81% of its own weight of the vapor. Experiment showed that there was 14% by weight of benzene in the air stream.

TABLE II

Per cent of Benzene Vapors by Weight in Air Stream

(320 c.c. per minute) saturated at 12.5° C.

Time in Minutes	Weight 320 cc of Air at 25° C. and 747 m/m Pressure	Weight of Benzene	Per cent by Weight of Benzene in Air	Average
1	0.3897 gr.	0.0670 gr.	14.67%	14.64%
2	0.7795 gr.	0.1325 gr.	14.52%	

These results were obtained by placing a weighed gel tube filled with an active gel in the adsorption train and passing air saturated with benzene vapors at 12.5° C. through it at the rate of 320 c. c. per minute until the first traces of benzene could be detected by smell. It was found that for a fifteen gram sample of gel it required less than three minutes.

TABLE III

Benzene Adsorbed by Commercial Silica Gel

Air Stream (320 c.c. per minute) saturated with

Benzene Vapors at 12.5° C.

Number of Run	Temperature of Saturator	Temperature of Adsorption Bath	Grams of C_6H_6 Adsorbed per Gram of Gel
1	12.5° C.	25.0° C.	.2788
2	12.2° C.	25.3° C.	.2765
3	12.5° C.	25.0° C.	.2790

When a gel of silicic acid of such a concentration that it required at least an hour's time to set is observed under a beam of light incident to the surface of the gel at an acute angle, bright refractive lines are seen to form slowly becoming feathery with much branching, as setting proceeds. These lines have been commented on by Roberts,[37] working in Graham's[15] laboratory, who thought that they were due to a fungus growth. This seems doubtful, as they form not only on the surface but in the body of the setting gel, and reform almost immediately when distorted by rotation.

A series of gels was made, using equal volumes of sodium silicate solution having a specific gravity of 1.18 and hydrochloric acid, varying only the concentration of the acid. The process of drying, washing, and activication was identical throughout.

These gels were compared as to their capacity to adsorb benzene vapors at 25° C. from an air stream (320 c.c. per minute) saturated at 12.5° C. Table IV gives the summary of this work.

TABLE IV

Adsorptive capacity of different gels made with varying concentrations of hydrochloric acid.

Benzene adsorption at 25° C. from an air stream (320 c. c. per minute) saturated at 12.5° C.

Normality of HCl	Time of set in Minutes	Condition of Feather Lines	Grams of C_6H_6 Adsorbed per Gram of Gel
10.0	Immediately	Absent	0.15
7.5	15	Absent	0.18
5.0	45	Short unbranched	0.22
3.9	105	Feathery	0.245
3.0	300	Feathery	0.243
2.0	720	Feathery	0.18

It was found that a gel formed by decomposing a sodium silicate solution having a specific gravity of 1.18 by means of 3.9 N hydrochloric acid had the highest adsorptive capacity.

INFLUENCE OF THE EXTENT OF SYNERESIS UPON THE ACTIVITY OF SILICA GEL

Graham[16] was the first to state that the dominating quality of colloids is the tendency of their particles to aggregate and contract. In the gel state this contraction or syneresis still proceeds, causing separation of the water from the gel structure. Schwarz and Stowener[60] have shown that this contraction is not dependent upon evaporation, but will continue even if the gel is submerged in water.

A series of gels was made using the same concentration of hydrochloric acid (3.9 normal) and sodium silicate solutions (1.18 specific gravity) throughout. The following conditions were investigated: (1) The effect of drying a gel rapidly, as soon as set, either by means of a higher temperature 40 - 50° C. or by the rapid removal of moisture at room temperature effected by an air blast from an electric fan. (2) The effect of allowing syneresis to complete itself, in one case in which evaporation at room temperature was prevented and in the other in which there was no check on evaporation.

TABLE V

EFFECT OF SYNERESIS UPON THE BENZENE ADSORPTIVE CAPACITY OF A GEL

Air stream (320 c.c. per minute) saturated at 12.5° C. with benzene vapors.

Temperature of Adsorption Bath 25° C.

Method of Drying	Drying Operation	Time Required	Grams of C_6H_6 Adsorbed Per Gram of Gel
40° - 50°	As soon as set	30 minutes	0.14
Air blast 18°C.	As soon as set	30 minutes	0.12
Air blast 18°C.	Syneresis complete	5 days	0.46
Air blast 18°C.	Dried to glassy solid	8 days	0.33

It has been found that drying a gel rapidly before syneresis had started should be avoided, as there is apparently a mechanical injury to the gel structure due to the rapid removal of water resulting in a gel which when activated had relatively low porosity and mediocre adsorptive capacity for benzene vapors. It is thought that syneresis effects to a certain degree the final orientation of the colloidal particles. If this is allowed to proceed to completion, a gel of superior activity is formed. An arbitrarily selected point was chosen in the progress of the syneresis of a silicic acid gel which was defined as that at which syneresis was complete. This was said to be complete when a gel, which had been covered to avoid evaporation from the time it was mixed, failed to squeeze out any water during a twenty-four hour period. Under

usual laboratory conditions a gel (made from mixing equal volumes of sodium silicate (specific gravity 1.18) and 3.9 N hydrochloric acid and allowed to set in a shallow crystallizing dish) required five or six days to reach this point.

WASHING

The object of washing a gel of silicic acid should be to remove as much of the soluble electrolytes as possible without injuring the physical structure of the gel. A series of gels was made using equal volumes of 3.8 N hydrochloric acid and a sodium silicate solution having a specific gravity of 1.18. They were allowed to stand covered at room temperature until syneresis was complete, and then washed free of chlorides. Further drying was done at ordinary temperature. The gels were activated at the usual temperature.

TABLE VI

EFFECT OF THE USE OF HOT WATER IN WASHING A GEL UPON THE BENZENE VAPOR ADSORPTIVE CAPACITY

Air stream (320 c.c. per minute) saturated with benzene at 12.5°C.

Temperature of adsorption bath 2.5° C.

Method of Washing	Temperature of Water	Time Hours	Grams of C_6H_6 Adsorbed per Gram of Gel.
Refluxed	90° C.	12	0.300
Running Distilled H_2O	10° C.	24	0.462

Although no quantitative analysis was made, it was found that washing could be stopped with no loss of activity at the point where no further precipitate of silver chloride formed but while there was still enough chlorides present to give a translucent opalescence. Refluxing with hot water removed the chlorides rapidly but a loss in adsorptive activity for benzene vapors resulted if carried to the point at which there was no further trace of chlorides observable.

DRYING

The porosity of a gel of silicic acid depends largely upon the method in which the soft gelatinous gel is dehydrated. A freshly prepared gel in which syneresis has not commenced, if placed in the blast of an electric fan at room temperature, soon shows signs of rapid dehydration. The surface of the gel becomes covered with a multitude of fine checks and if this drying is continued the entire gel breaks up into fine pieces. These pieces, if washed free of chlorides and activated, showed a very low adsorptive capacity for benzene vapors.

Table VII shows the results of drying a series of gels in various ways. The gels were made using the standard concentrations (3.8 normal hydrochloric acid and an equal volume of sodium silicate solution having a density of 1.18). After syneresis was complete, the gels were washed in running cold distilled water until the washings were only slightly opalescent with silver chloride. After drying the gels were further activated as previously described at 200° C. and compared as to their adsorptive capacity for benzene vapors.

TABLE VII

EFFECT OF METHOD OF DRYING SILICA GELS UPON THE

BENZENE ADSORPTIVE CAPACITY

Air Stream (320 c.c. per minute) saturated with benzene at 12.5° C.

Temperature of adsorption bath 25° C.

Method of Drying	Time of Drying	Grams of C_6H_6 Adsorbed per Gram of Gel
18°- 25° C. in still air	72 hours	0.330
40°- 55° C. " " "	24 "	0.260
7 inch fan 18° C.	36 "	0.460
18 " " " "	12 "	0.260

The ill effects of rapid drying are not confined to unwashed gels but have been observed in Cl^- free gels in which syneresis has been completed. There is apparently a mechanical injury to the gel structure due to the rapid removal of the water. A moderate blast of air at room temperature however, if it is so controlled that there is a uniform shrinking of the gel pieces unaccompanied by any checking of the surface, results in a very active gel.

A seven inch electric fan was used for the purpose of drying the gels, it being arranged so that the blast was directed downwards. Different methods of placing the gels in this blast were tried, using cheese cloth racks, shallow evaporating dishes, and glass jars six inches deep. It was found that if the gel pieces were spread out on the cheese cloth racks, that drying took place much too rapidly. The best results were obtained by drying the gel in the glass jars. These glass jars were

later replaced by a large rectangular glass vessel having five inch walls. The gel lumps were spread out on the bottom of this dish in a layer approximately 3 cm. thick. Under these conditions it required nearly thirty-six hours to dry 1800 grams of fresh gel to a point where no further change in volume occurred.

One of the factors in drying a gel, which is usually beyond the control of the average laboratory, is the relative humidity of the air. It has been found that much more active gels have been produced during rainy periods than otherwise. As a means of correcting this difficulty, it was found that if a ten inch evaporating dish filled with water was placed near the fan, better results were secured.

ACTIVICATION

The process of activating silica gel consists essentially of removing the excess of water held in the capillaries. It has been found by Patrick[61] that for the adsorption of sulphur dioxide there was a minimum limit for the amount of water held by the gel beyond which there was a loss in activity. J. von Bemmelen[62] has shown that as the temperature of activication is raised, there is a decided loss of adsorptive activity as soon as the gel particles show signs of sintering. Holmes[4] in a recent contribution stated that the amount of water lost at 200° C. was almost the same as at 150° C. Ruth,[50] working in this laboratory, has demonstrated that there was a progressive loss in adsorptive capacity for dry ammonia gas as the temperature of activication was raised above 250° C.

The effect of the temperature of activication upon the adsorptive capacity of a very active gel for benzene was investigated. The results are given in Table VIII.

TABLE VIII

EFFECT OF THE TEMPERATURE OF ACTIVICATION UPON THE ADSORPTIVE CAPACITY OF SILICA GEL FOR BENZENE VAPORS

Air stream (320 c.c. per minute) saturated with benzene vapors at 12.5° C.

Temperature of adsorption bath 25° C.

Temperature of Activication	Grams of Water Adsorbed Per Gram of Gel	Grams of C_6H_6 Adsorbed Per Gram of Gel
25° C.	0.150	0.320
110° "	0.080	0.380
150° "	0.072	0.462
250° "	0.070	0.460
300° "	0.068	0.430

The same precautions in activating a fresh sample of silica gel must be observed that have been established in drying the recently prepared soft gel. The preliminary temperatures must be low and a too rapid dehydration must be avoided.

DISCUSSION

The factors influencing the physical structure of silica gel have been found to depend largely upon the mode and extent of syneresis

and also upon the method of drying.

Washing a crude gel free of its acid and salt after syneresis had reached completion produced a very active gel. This gel had an adsorptive capacity for benzene vapors of 0.462 grams of benzene per gram of gel, while one dried to a rigid solid in the open at room temperatures before washing had an adsorptive capacity of 0.330 grams of benzene per gram of gel.

It has been found that an active gel can be produced by drying at room temperatures by means of the air blast from an electric fan. The force of the air blast should be so regulated that there is a gradual shrinkage of the gel particles and that no checking of the gel surface occurs.

For the adsorption of benzene vapors, there is no gain obtained by activating the gel at temperatures above 200° C.

The concentration of the acid and water glass solutions used in preparing the gel should be such that it requires an appreciable time (at least an hour) for the gel to set. This effect is probably due to the fact that the colloidal aggregates can better orientate themselves into a homogeneous structure.

Prolonged washing with hot water in order to remove all traces of chlorides tends to lower the adsorptive capacity of a gel.

THE AMMO GEL OF SILICIC ACID

In the first part of this discussion of the factors influencing the activity of silica gel, only those have been considered which affected its physical structure per se.

The two factors influencing adsorptive activity are, of course, the extent and the nature of the surface. Various methods have been used to change the nature of the surface. Patrick[63] has developed methods of depositing metallic colloids on the surface of the gel and in this way radically change the properties of the gel. Bohringer and Schwarz[64] have produced a highly dispersed colloidal sol of silica by dissolving silica in aqueous ammonia.

Ammonium silicate has not been isolated as a solid although Struckman[65] has shown that gelatinous silica is soluble to the extent of 0.02 grams per 100 grams of a 5% solution of ammonium carbonate. Schwarz[66] has found that the solubility of silica in aqueous ammonia depended upon the concentration and temperature of the ammonia and also upon the physical conditions of the silica. Schwarz and Liede,[67] using quartz vessels to avoid contamination by the alkalies from glass, found that in a concentrated solution of ammonia equilibrium was established in seventy-two hours, that 64% of the silica was in actual solution, 8% in a colloidal dispersion, and 28% undissolved.

The gelatinous precipitate produced by Struckman[65] by adding an ammonium carbonate solution to one of sodium silicate, when thoroughly washed free of carbonate ions, retained 0.78% of ammonia after being thoroughly air dried. Liebig[68] claimed however that all of the ammonia could be washed from the gel. Schwarz[66] has stated that it is difficult to determine whether the ammonia neutralizes the silicic acid or forms an adsorption complex with it.

It has been found in this laboratory that a gel possessing unusual qualities can be produced by treating a crude gel after syneresis

was complete with concentrated aqueous ammonia, and after permeation, which should not exceed two hours, washing the gel free of chlorides. The following method of preparing this ammo gel has been found to give the most satisfactory results.

To a 3.8N solution of hydrochloric acid an equal volume of a water glass solution having a specific gravity of 1.18 was added with vigorous agitation by means of compressed air. The water glass used in this work was a water-white product having an original specific gravity of 1.402 and an Na_2O : SiO_2 ratio of 1:3.46.

The hydrosol of silicic acid formed in this way was poured into shallow crystallizing dishes so that the layer of gel formed was not more than three centimeters thick. The dishes were then covered with large watch glasses to prevent excessive evaporation and allowed to stand until syneresis was complete. This point was arbitrarily selected as that at which no more liquid was squeezed from a covered gel during a twenty-four hour period. The concentration of water glass and hydrochloric acid used in this work required from three to four hours to set and syneresis was complete within seven days.

When syneresis was complete, the gel was broken into lumps with edges approximately three centimeters long, placed in a wide mouthed bottle, and covered with a concentrated solution of ammonium hydroxide having a specific gravity of 0.90, containing 255 grams of NH_3 per liter. At the end of the first half hour the ammonium hydroxide solution was decanted and replaced with fresh.

The ammonium hydroxide penetrated the gel pieces uniformly as was evidenced by the changing color. The yellow green color of the orig-

inal clear gel was replaced by the opalescent appearance of the ammo-gel. After a period of not more than two hours, at which time even the largest gel pieces had been invaded by the ammonia, the solution was poured off and the gel placed in a dry rack.

The terminology contributed by Graham[15] to the science of colloid chemistry has been preserved largely in its original form. It has been thought best to follow his lead in terming the gel produced by treating the unwashed hydrochloric acid gel of silicic acid with concentrated ammonia an ammo gel of silicic acid.

The activity of this gel depends to a great extent upon the method of drying. To prevent too rapid drying the gel pieces should be spread upon the bottom of a container having sides of at least five inches in a layer not less than five centimeters thick. If the gel is properly dried, the pieces will show an uniform shrinkage with no checking of the surface. During the process of drying there is a definite cycle of changes in the physical appearance of the gel. The bluish opalescence of the fresh ammo gel disappears, followed in turn by a condition in which the surface of a fresh fracture is dull; this is again followed by a stage in which the fresh fracture has a bright glassy appearance. If the gel is dried much beyond this stage, the concentration of the salt solution held in the capillary spaces increased to such a point that crystallization takes place <u>in situ</u>, shattering the gel pieces and injuring its activity.

Washing is started when the majority of the gel pieces show this glassy fracture. Due to the fact that a silica gel so treated with ammonium hydroxide is soluble in hot water, all of the washings should be done with cold water. As the chloride content of the gel falls to a certain level, which varies with the mode of drying, the solubility of the

ammonium silicate increases and the point at which the preliminary washing should stop is that at which there is only a slight cloudiness of silver chloride after the ammonium silicate has dissolved with an excess of nitric acid.

The citron yellow precipitate formed when a solution of silver nitrate is added to a solution of a soluble silicate is, according to Hawkins,[69] silver meta silicate, Ag_2SiO_3. As this silver silicate is decomposed by nitric acid, the procedure in testing for chlorides to follow in washing these gels is to add nitric acid to the test solution after the addition of the silver nitrate. The amount of ammonium hydroxide in the wash water is relatively very small, and consequently the amount of silver chloride which it would dissolve is below that of the minimum concentration of chloride necessary to inhibit the solubility of the ammonium silicate.

Washing is stopped at the point where a decided yellow precipitate is formed, and the gel further dried until it reaches its final degree of hardness. During this final drying, the gel passes from a clear water-white appearance to an opaque condition which finally changes to a clear bluish opalescence.

If the maximum amount of chlorides consistent with the solubility of the ammonium silicate has not been removed, some of the larger gel pieces will not pass into the final clear stage, but will remain opaque. A final washing with iced, distilled water will correct this.

PHYSICAL PROPERTIES OF THE AMMO-GEL OF SILICIC ACID

The gel, prepared by treating a crude silica gel after syneresis is complete with concentrated aqueous ammonia, is a clear opalescent substance somewhat softer than the ordinary silica gel. When ground to a fine powder, there is a decided increase in the apparent volume due either to the adsorption of air or to some influence of the ammonia. This can be demonstrated by heating some of the powder in vacuo to a temperature of 150° C., at which temperature it loses its fluffiness and occupies relatively the same apparent volume as that of the untreated gel.

The action of the dehydrated gel in water differs from the Patrick gel in that, instead of an obvious displacement of air by the water accompanied by a decided splitting of the gel particles, there is scarcely any displacement and the water permeates the gel structure uniformly without splitting. The fact that water does not displace air from the dehydrated gel strengthens the contention that the ammonia has entered into the structure of the gel.

When strongly heated over a blast flame, the ordinary silica gel splits and swells into a bright "pop-corn" appearance, apparently due to the sintering of the silica. The ammo-gel, however, when heated does not swell but, instead, loses volume and assumes a dull, lusterless form. The ash of silica gel is slightly acidic to methyl orange, while that of ammo-gel is alkaline to phenolphthalein.

INVESTIGATION OF THE ADSORPTIVE PROPERTIES OF AMMO-GEL

The outstanding property of this ammo-gel is its ability to decolorize aqueous solutions of basic dyes, especially methylene blue. The methylene blue solution used in this work was of a 400th molar concentration, prepared from a high-grade zinc-free sample.

The gel, activated at 150° C., was so pulverized that it would pass through a 200 mesh sieve and kept in ground glass stoppered bottles until used. A half gram sample was weighed in an 100 c.c. Erlenmeyer flask and the methylene blue solution added to it from a burrette. The flask was then stoppered with a cork which had been previously impregnated with paraffin. After vigorous shaking for two minutes, the solution was poured onto a #3 Whatman filter paper and the filtrate caught in a clean test tube the dimensions of which were 2 x 17 cm. Complete decolorization was defined as that of a solution in which no color could be detected looking through a column eight centimeteres long in a standard dimension test tube towards a "day-light" screen.

Table IX shows a comparison of the decolorizing properties of Norite, ammo-gel, and silica gel (Patrick).

TABLE IX

Adsorbent used	Amount	Cubic Centimeters of 400th Molar Methylene Blue Sol.	Degree of Decoloriz.
Silica Gel	10 grams	5	Partial
Norite	0.5 "	55	Complete
Ammo-gel	0.5 "	45	Complete

Because of the retention of an appreciable amount of free ammonia by the activated gel, it was thought that the decolorization might be due to this factor. The addition of a concentrated aqueous solution of ammonia to the methylene blue solution only intensified the purple tint of the dye.

If washing is continued to any extent after the chlorides have been removed, the gel particles become more opalescent, finally reaching a condition in which they are no longer translucent. With this increase in the opalescence of the gel, there is a progressive falling off of its adsorptive capacity for benzene vapors, but this is not accompanied by a marked decrease in its decolorizing capacity.

Another factor that effects the benzene adsorption but has no effect upon the decolorization capacity of the gel is age. If a tightly stoppered bottle containing activated gel is allowed to stand for several weeks, it has been found that at the end of this period the benzene adsorptive capacity has fallen off by at least 50% while there has been only a loss of 4.5% in the decolorization capacity.

Table X gives the results of the effect of aging of an ammogel upon the decolorizing and benzene adsorptive capacity.

TABLE X

Age	C.c. of Methylene Blue 400th Molar Solution Decolorized by 0.5 Grams of Gel at 25° C.	Grams of C_6H_6 Adsorbed per Gram of Gel from an Air Stream 320 c.c. per minute, saturated at 12.5° C., adsorbed at 25° C.
Fresh	45 c.c.	0.36
1 Week	45 "	0.32
2 Weeks	40 "	0.28
4 Weeks	35 "	0.26
8 Weeks	35 "	0.18

The effects of treating a freshly prepared silica gel with concentrated aqueous ammonia are very marked, simulating those of syneresis in many ways. There is a decided shrinkage in volume accompanied by an increase in hardness, but the activity of a gel so treated does not compare in any way with one in which syneresis has been allowed to proceed in a normal manner.

Table XI summarizes the effects of different treatments upon the adsorptive capacity of ammo-gel for benzene and water vapor together with its decolorizing action upon a 400th molar methylene blue solution. In the case of water vapor, air at the rate of 320 c. c. per minute was saturated with water at 18° C. and passed through the gel maintained at a temperature of 25° C.

TABLE XI

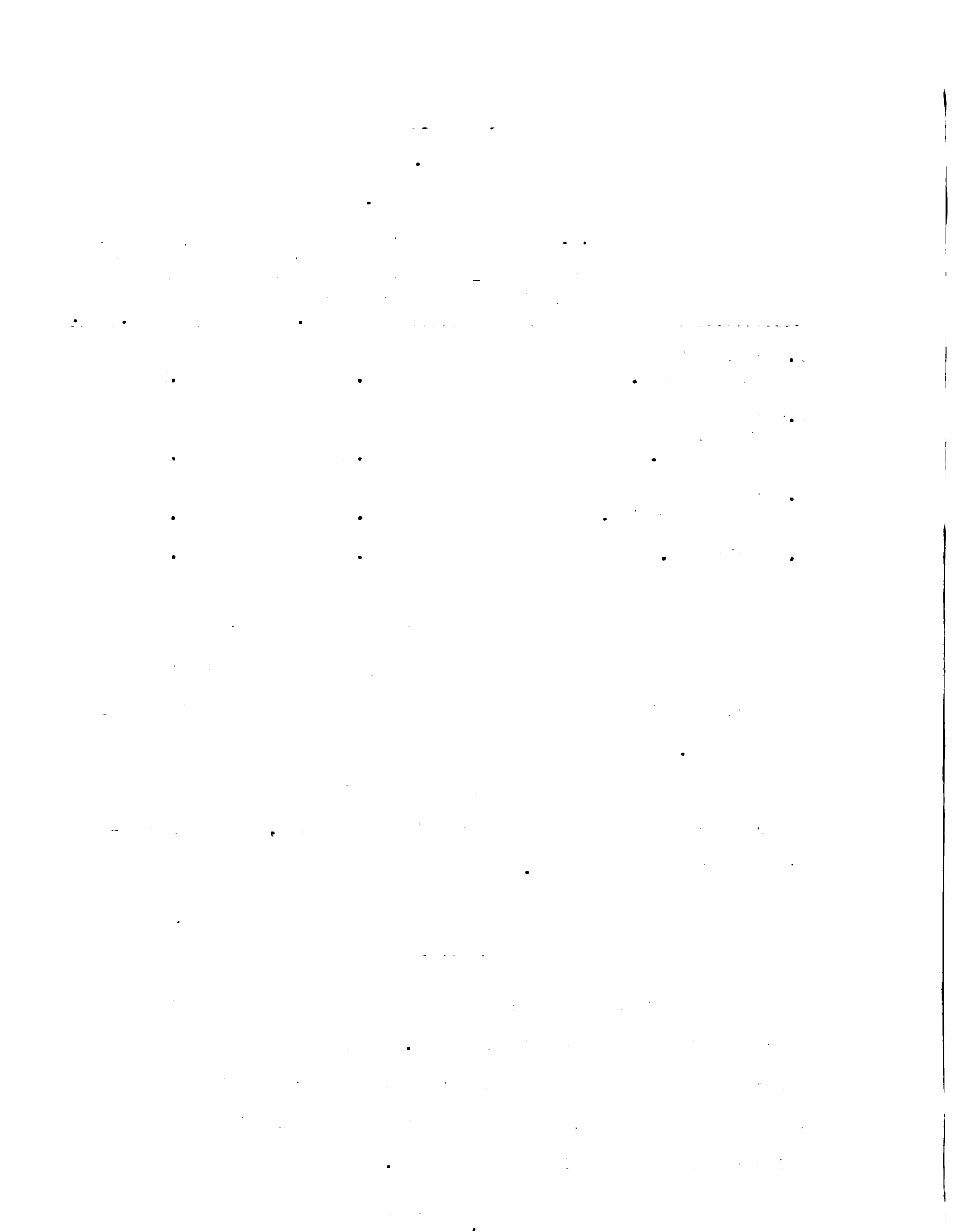
ADSORPTION OF VAPORS AT 25° C. BY AMMO-GELS PREPARED BY DIFFERENT METHODS.

Method	C.C.400th Molar Methylene Blue Solution Decolorized	Grams of Water Adsorbed per Gram of Gel from Air Saturated at 18° C.	Grams of Benzene Adsorbed per Gram of Gel from Air Saturated at 12.5° C.
1. Treated with NH_3 as soon as set.	22	0.18	0.12
2. Treated with NH_3 after completion of syneresis.	45	0.42	0.38
3. Treated with 6N HNO_3 after dehydration.	3	0.68	0.24
4. Patrick Gel.	2	0.38	0.28

It was thought that the mechanical advantages gained by the peptizing action of the ammonia upon the fresh gel might be retained and the further action of the ammonia checked by treating the ammonified gel with an acid. Investigations of this treatment were carried out and it was found that while the adsorptive capacity of the gel for benzene and water vapors were enhanced by neutralizing the ammonia, the decolorization capacity was eliminated.

SUMMARY

The effect of a concentrated solution of aqueous ammonia upon a crude silica gel has been investigated. This has shown that while the adsorptive capacity for benzene vapors of the dehydrated gel have not been materially changed, there has been a decided change in the decolorizing capacity for solutions of basic dyes.



The effect of acid upon this ammonified gel has been to destroy the decolorizing properties but to enhance its adsorptive capacity for water vapors. There has been shown that there is a progressive decrease in the adsorptive capacity of the ammo-gel for benzene vapors with age.

The decolorizing action of these ammo-gels is directly correlated with the presence of ammonia in the gel structure. The apparent relation between pore size and decolorizing action is not clear since a gel such as No. 1, Table XI, with a poor adsorptive capacity for benzene vapors still shows a relatively high decolorizing activity when compared with the ordinary gel.

BIBLIOGRAPHY

1. W. A. Patrick, Inaugural Dissertation, Gottingen (1914); U. S. Patent 1,297,724 (March 18, 1919); 1,335,348 (March 30, 1920).
2. H. Briggs, Proc. Roy. Soc., 100A, 88-92 (1921).
3. H. A. Fells and J. B. Firth, J. Phys. Chem., 29, 241,249 (1925).
4. H. N. Holmes, J. Ind. Eng. Chem., 17, 280-282 (1925); 18, 386-388 (1926).
5. R. Fruhling, Chem. Z., 19, 117-121 (1895).
6. P. Walden, Z. Koll., 6, 233-235 (1910).
7. A. Baume, Chymie experimental et raisonne, (Paris) 1, 329 (1773).
8. H. Watts, Dictionary of Chemistry, 3rd Edition, page 240 (1883).
9. A. Noble, Proc. Norwich Soc., 1867.
10. J. J. Berzelius, Lehrbuch der Chemie (Dresden) 2, 122-126 (1833); Ann. Chim. Phys. (2) 14, 366-370 (1830).
11. J. J. Ebelman, Ann. Chim. Phys. (3) 16, 129-131 (1846).
12. A. C. Becqueral, Compt. Rend., 53, 1196-1202 (1861).
13. M. Kroger, Koll. Z., 30, 16-18 (1922).
14. J. F. Spencer and K. Proud, Koll. Z., 31, 36-40 (1922).
15. T. Graham, Phil. Trans., (London), 151, 181-224 (1861).
16. T. Graham, J. Chem. Soc., 15, 246-254 (1862); J. Chem. Soc., 17, 618-626 (1864).
17. J. Tyndall, Proc. Roy. Soc., 17, 223-226 (1869); Phil. Mag., (4) 37, 384-387 (1869); Proc. Roy. Inst., 6, 365,367 (1871).
18. E. M. Plessey, Compt. Rend., 41, 599-603 (1855).
19. E. Monier, Compt. Rend., 85, 1053-1054 (1877).

20. S. Meunier, Compt. Rend., 112, 953-954 (1891).

21. H. N. Holmes, J. Phys. Chem., 22, 510-519 (1918).

22. H. N. Holmes, J. Am. Chem. Soc., 41, 1329-1333 (1922).

23. Gmelin-Kraut, Handbuch der anorganische Chemie (Heidelburg), page 143 (1912).

24. W. Flemming, Z. Phys. Chem., 41, 427-457 (1902).

25. E. Jordis, Z. anorg. Chem., 44, 200-207 (1905).

26. R. Zsigmondy and W. Heyer, Z. anorg. Chem., 68, 169-187 (1910).

27. M. Wunder and A. Suleimann, Am. Chem. Anal., 19, 45-49 (1914).

28. J. M. von Bemmelen, J. Prak. Chem., 23, 324-326 (1881); Ber., 13, 1466-1469 (1880).

29. E. Jordis, Z. Electrochem., 11, 835-841 (1905).

30. E. Jordis and E. H. Kanter, Z. anorg. Chem., 35, 16-22 (1903).

31. F. Mylius and E. Groschuff, Ber., 39, 116-125 (1906).

32. V. Lenher and H. B. Merrill, J. Am. Chem. Soc., 39, 2630-2635 (1917); V. Lenher, J. Am. Chem. Soc., 43, 391-393 (1921).

33. J. W. Mellor, A Treatise on Quantitative Inorganic Analysis, (London) page 175 (1913).

34. E. Fremy, Ann. Chim. Phys., (3) 38-42; 326-331 (1853).

35. L. Doveri, Ann. Chim. Phys., (3), 21, 40-43 (1847); Liebig's Ann., 54, 256-259 (1847).

36. J. N. von Fuchs, Liebigs Ann., 82, 119-123 (1852).

37. C. Roberts, J. Chem. Soc., 21, 274-277 (1868).

38. J. M. von Bemmelen, J. Prak. Chem., (2) 23, 324-326 (1881); Z. anorg. Chem., 13, 233-356 (1896); Z. anorg. Chem., 18, 14-36 (1898); Z. anorg. Chem., 18, 98-146 (1898); Z. anorg. Chem. 30, 265-279 (1902);

Z. anorg. Chem. 36, 380-402 (1903); Z. anorg. Chem. 59, 325-347 (1908); Z. anorg. Chem. 62, 1-23 (1909); Chem. Week-b., 6, 63-82 (1909).

39. E. Jordis, Z. angew. Chem., 19, 1697-1702 (1906).

40. R. Zsigmondy, Z. anorg. Chem., 71, 356-377 (1911).

41. T. Carnelley and J. Walker, J. Chem. Soc., 53, 59-101 (1888).

42. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry (London), 6, page 293 (1925).

43. E. M. Faber and H. G. Olson, Chem. Met. Eng., 28, 805-806 (1923).

44. G. Tschermak, Z. Phys. Chem., 53, 349-367 (1905); Z. anorg. Chem., 55, 101 (1907); Zentralblatt Min. Geol., 225-230 (1908); Z. anorg. Chem., 63, 230-274 (1910).

45. O. Mugge, Centr. Min., 129-134 (1908).

46. O. Suida, Setzber Akad. Wien., 113, 725 (1904).

47. A. Sabeneff, J. Russ. Phys. Chem. Soc., 21, 515-525 (1890), 23, 80-91 (1891).

48. J. S. Anderson, Z. Phys. Chem., 88, 191-228 (1914).

49. E. Berl and W. Urban, Z. angew. Chem., 36, 57-62 (1923).

50. B. F. Ruth, M. Sc. Thesis, Mich. State College (1925).

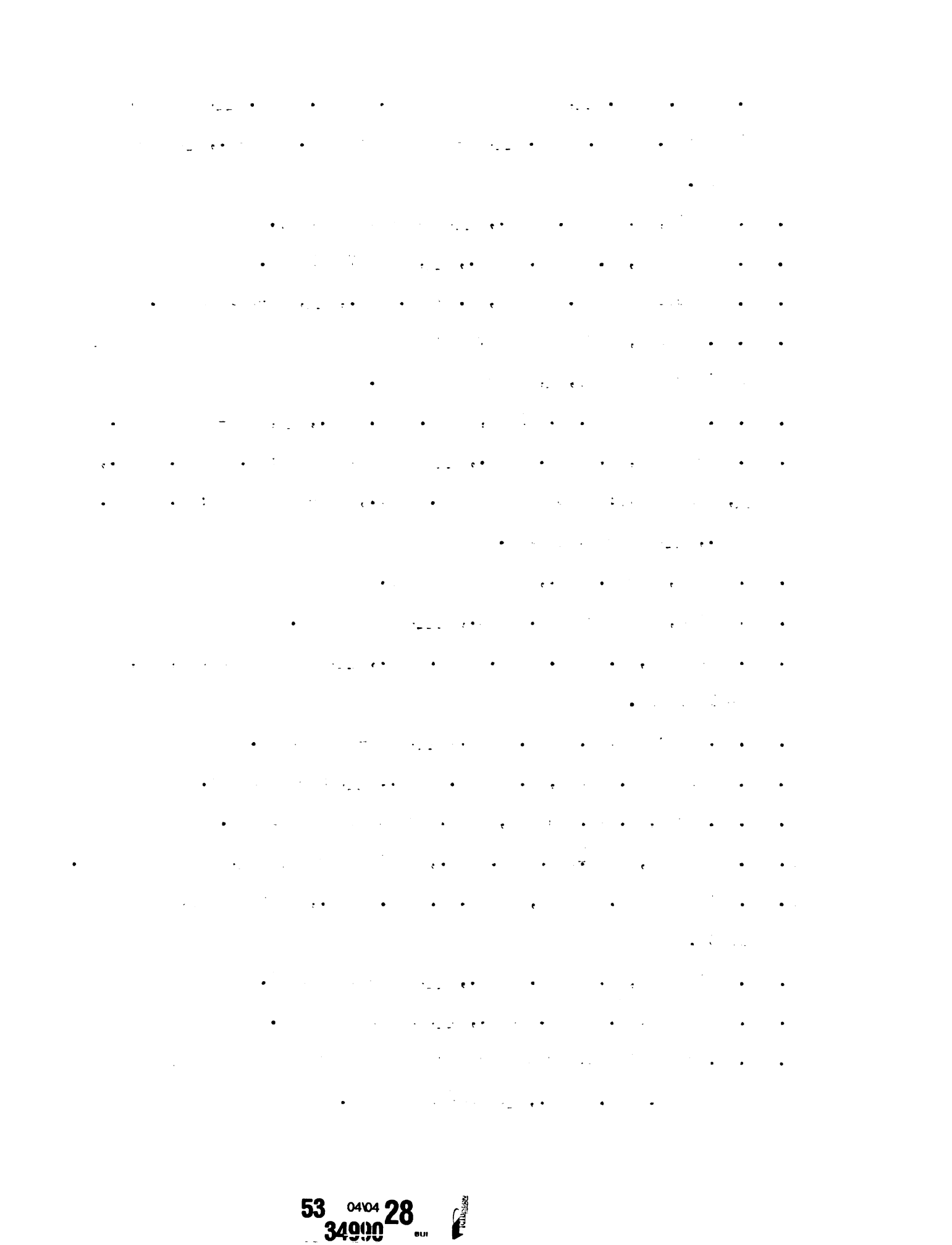
51. O. Butschli, Verh-Nat. Med. Ver., (Heidelburg) (2) 6, 287-301 (1901).

52. W. Biltz and W. Geibel, Nachr. K. Ges. Wiss., (Gottingen), 141-156 (1906).

53. R. Zsigmondy, Z. anorg. Chem., 71, 356-377 (1911).

54. W. Bachmann, Z. anorg. Chem., 73, 125-172 (1911).

55. P. P. von Weimarn, Grundzuge der Dispersoidchemie (Dresden) page 30 (1911) Rev. Gen. Coll., 2, 193-195 (1924).


53 04\04 28
34900

56. N. Pappada and C. Sadowsky, Z. Koll., 6, 292-297 (1910).

57. H. C. Chatelier, Compt. Rend., 147, 660-662 (1908).

58. J. M. von Bemmelen, Z. anorg. Chem., 18, 98-146 (1898).

59. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry (London), 6 pages 304-307 (1925).

60. R. Schwarz and F. Stowener, Koll. Beiheft., 19, 171 (1924).

61. W. A. Patrick, J. Am. Chem. Soc., 42, 946-978 (1920).

62. J. M. von Bemmelen, Arch. Neer. Sci. exact Nat., (2) 6, 607-624 (1901).

63. W. A. Patrick, British Patent, 212,034 (1923); 212,035 (1923).

64. C. F. Boehringer and R. Schwarz, German Patent D.R.P. 373,110 (1920).

65. C. Struckmann, Liebig's Ann., 94, 341 (1855).

66. R. Schwarz, Ber., 49, 2359 (16) 52B, 601 (1918).

67. R. Schwarz and O. Liede, Ber., 53B, 1509-1513 (1920).

68. J. von Liebig, Liebig's Ann., 94, 375 (1855).

69. J. D. Hawkins, Am. J. Science, (3) 39, 311-312 (1890).