THE EFFECTS OF HYDRATED FERRIC OXIDE ON THE ADSORPTIVE CAPACITY OF SILICA GEL

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INTRODUCTION

It has been found that if an aqueous solution of a silicate be treated with the equivalent quantity of an acid, free silicic acid and a salt are formed. This silicic acid is in the colloidal state, and not in the form of a simple dissolved substance. If this system be allowed to stand undisturbed, the silicic acid present will exhibit its insolubility, and a gel will form sooner or later unless the mixture is very dilute. The speed of gelation depends upon several factors, among which are, excess of acid or alkali present, temperature, agitation, the kind of acid used, and many others, all of which contribute to the final properties of the gel.

Considerable investigation has been carried out regarding silicic acid gels both with respect to their preparation and their properties. It was found that the gel upon drying exhibited the remarkable property of holding certain substances on its surface. This property had been observed in many other substances, among which was a diatomaceous earth or Kieselghur,[1] found in marine deposits in many localities and consisting of siliceous skeletons of diatoms, the silica of which was derived from the water in which the diatoms lived. This earth was used as a decolorizer, and will absorb several times its weight of water.

The peculiar property exhibited by the dried silicic acid gel of holding foreign substances on its surface, is known as adsorption, as distinguished from absorption. Inasmuch as this property is important from both the scientific and commercial standpoints, much research has been done with the view of discovering, if possible, the best method of preparing a gel which will exhibit maximum adsorption.

Adsorption appears to be largely a physical phenomenon[2] and is influenced in many ways. All silicic acid gels exhibit this property to a greater or less degree, which property varies with the method of preparation. In view of the fact that the variations in preparation of gels are practically infinite, and that even after the gel has been obtained conditions of drying have a tremendous effect on the adsorptive capacity, it is not surprising that many contradictory reports have been published regarding silica gel.

Holmes,[3] in 1918, found that by varying the concentration of hydrogen and hydroxyl ion, he could control the speed of gelation. In his researches he prepared a valuable 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 given ratio of Na_2O - SiO_2 will produce a gel which will set in any length of time desired.

Graham[4] produced a hydrosol of silicic acid by mixing together equal volumes of ten per cent solutions of sodium silicate and hydrochloric acid. He then purified the hydrosol by dialysis, using his famous hoop dialyzer. Though some work had been done before his time on this subject, no systematic research is evident, so the history of silica gel should properly date from the experiments of Graham.

Gels have been prepared at a much earlier date than those prepared by Graham, though their nature was but vaguely suspected. In 1773 Baume believed that he had obtained a soluble form of silica by treating <u>silicium liquor</u> with different acids. Berzelius, in 1830, prepared gels in several different ways, among which he evaporated a mixture of SiF_4 and H_2O, which finally set to a gel. Ebelman, in 1845, made a gel by hydrolysis of ethyl ortho silicate. In 1861, Becqueral produced a gelat-

inous silica by electrolysis of potassium silicate. Plessy, in 1855, produced a gel using a silicate and acetic acid. Others, including Monier (1855) and Meunier (1891), have prepared gels of silicic acid by various methods.

Holmes and Anderson[5] have prepared a silica gel by precipitating silica and oxides of iron together and then dissolving the iron out of the gel by acids. They claim that this gives a very active gel due to the effect of the iron oxides on pore formation.

Patrick and McGavack Jr.,[6] after a series of experiments with SO_2 and silica gel, decided that the ease with which a gas condenses, promotes adsorption. At that time they held the theory that moisture content of the gel determined its activity as an adsorbent.

Heat of wetting was studied by Patrick and Grimm,[7] by immersing the gel in different liquids. They account for the heat liberated by a decrease in surface energy due to diminution of interfacial tension between the structural water of the gel and the liquid employed for immersion.

Patrick and Davidheiser[8] investigated the adsorption of NH_3 by silica gel with the purpose in view of studying the nature of the small amounts of water left in the gel after activation. They concluded that the water content had but little effect, as they produced a gel containing as low as 0.33% H_2O which was but slightly less active than those containing considerably larger amounts.

Holmes, Kaufmann, and Nicholas[9] studied the vibrations in gel columns, and found that vibration frequency varies directly as the concentration of silicic acid, increasing with mineral acids and decreasing with organic acids.

Several authors have succeeded in obtaining crystals from both the hydrosol and hydrogel of silicic acid. This was accomplished at higher temperatures however, and after prolonged heating. Though these crystals have been formed at high temperatures, they would undoubtedly form at ordinary temperatures, though very slowly. It is believed that vein quartz was formed by a gradual process of dehydration, as a convincing part of this process can be reproduced in the laboratory. Many gems are probably formed in the same manner. Silicic acid in a more or less hydrated form occurs in nature as opal, chalcedon, agate, hydrophane, etc., and in the vegetable kingdom as tabashir. Hydrophane and tabashir closely resemble artificial gels, being more or less transparent, according to water content. Liesegang has shown that agate has probably been produced from a gel of silicic acid into which layers of iron and other salts have penetrated. To the geologist a working method of duplicating many such processes of nature, is of great value.

Under ordinary conditions the silicic acids are of the weakest of inorganic acids. Orthosilicic acid readily becomes converted into its anhydride and water, this being readily facilitated by heating. Much investigation has been carried out to determine the exact composition of the hydrated silica. Graham[10] found that by careful drying of the purified hydrosol of silicic acid in vacuo, and further drying over concentrated H_2SO_4, the resulting product had a composition corresponding to the formula $SiO_2.H_2O$. This was later verified by C. Roberts[11] in 1868. Various hydrates have been obtained in different manners, corresponding to the formulas $2SiO_2.3H_2O$, $3SiO_2.2H_2O$, $3SiO_2.H_2O$, and $4SiO_2.H_2O$. Carnelley and Walker[12] found that in dehydrating a sample of carefully prepared silicic acid gel, there was such a slight change in the rate at which water was given off, that the belief in the existence of any definite hydrate was

not justified. They further concluded that silica is a polymeride with the formula $(SiO_2)_n$. The value of n was found by Sabeneeff[13] to lay between 800 and 1000, which would give the molecular weight of this compound an extremely large value. This is meaningless because of the heterogenity of the colloid system, which systems do not follow the laws of osmotic pressure.

Mellor[14] believes that the hydrates of silicic acid are but arbitrarily selected states in a continuous series between the hydrosol and the dehydrated silica, and are represented by points on a continuous drying curve.

In his study of colloidal metallic oxides, SiO_2 received special attention from Van Bemmelen[15]. His investigations of the physical properties of silica gel included the equilibrium conditions existing between the weight of water held per gram of SiO_2 and the vapor pressure. He established a hydration-dehydration curve from which he concluded that the hydrogel of silicic acid is of an unstable composition of the general composition $SiO_2.nH_2O$, the value of n depending on the previous history of the gel.

The structure of silicic acid gels has been the object of considerable investigation for many years. Frankenheim in 1835 believed jellies to be aggregates of small crystals with pores between them. K. Von Nageli in 1879 adopted a similar view that gels were composed of molecular complexes or micellae, with crystalline properties, separated by skins of H_2O and forming interstices in which H_2O was contained by molecular attraction. Freundlich[16] agrees closely with this view, considering gels to be the same as sols, in which solid particles are so abundantly present, that the dispersion medium, the liquid, is reduced to very thin films, which, like a foam, separate the closely packed particles. Van Bemmelen believes that the colloidal particles of silicic acid arrange themselves

with the water molecules to form a cell-like structure of definite constitution, and that these cells hung together at certain points to form a network. Butschli held a similar view to Van Bemmelen, but in 1911 this theory was disproved by Zsigmondy who examined with the ultramicroscope a dry gel which had been treated with benzol vapors. As the benzol evaporated, the Tyndall cone[17] appeared, and faintly discernible submicrons, which grew in brightness, were seen. These submicrons became so bright that they illuminated their neighboring particles. This light was linear polarized. Bachmann, in 1917, found by his vapor pressure isotherms, that the pores of silicic acid gels have radii between 2.5 and 5 millimicrons, which is about 300 times smaller than Butschli's honeycombs. These experiments explain Van Bemmelen's hysteresis cycle. Zsigmondy and Bachmann favor a fibrillar structure. McBain (1920) holds a view similar to Freundlich[16] and Patrick[7], that identical colloidal particles are present in the sol and gel state, which differ only in mechanical rigidity and elasticity. Bradford[18] summarizes the different hypothesis concerning gel structure held by various investigators, and classifies the different systems under which gels fall.

The tendency exhibited by all solids to condense upon their surfaces a layer of any gas or liquid with which they may be in contact is termed adsorption. The amount of adsorption is conditioned primarily by the extent of surface exposed[19]. Since most charcoals exhibit great surface due to porosity, considerable work has been done with this substance. In certain technical processes silica gel competes with activated charcoal, so at the present time there is a distinct difference of opinion as to the relative merits of each as an adsorbent.

Patrick was among the first to investigate the adsorption of gases by silica gel[6][8]. Daniels and McCollum[20] propose to adsorb

nitric oxide with silica gel in the arc process for the fixation of nitrogen. The Royal Dutch Shell Company of San Francisco, California, has successfully employed activated silica gel to remove sulphur compounds from oil and to recover gasoline vapors[21]. Gasoline purified by silica gel was found to be much superior to that prepared in the ordinary manner[22], when used as a motor fuel. Ray[23] found that ordinary silica gel only takes up 23% of its weight of benzene. Holmes[24] states that he produced a very active gel by treating sodium silicate with nickel chloride. This gel, he reports, will adsorb 100% of its weight of benzene. Briggs[25] prepared a gel by a special process which at -190° C had an adsorption capacity 60% greater for nitrogen than the best charcoal known. Silicic acid gels have been used as a vehicle for metal catalysts. Reyerson and Thomas[26] prepared a gel by the Patrick method and after drying evacuated it at 250° C for two hours. It was then treated with pure hydrogen. After adsorption equilibrium had been reached, solutions of salts of the metals to be deposited were added. Gold, silver, platinum, palladium, nickel, and copper salts were used. Of these, palladium and nickel showed remarkable activity as a catalyst in the hydrogen-ethylene reaction.

The preceding brief review of the literature is not intended to cover the entire field. The papers considered were included for the reason that they appeared to have a direct bearing on the property of adsorption. In view of the fact that there are so many variations in the preparation of silica gel which affect this property, a method embracing the most desirable features of the many known methods should result in a superior gel.

The indication of the further possibilities of specially prepared silica gels led the writer to the consideration of the effects of ferric oxide on the adsorptive properties of silica gel. A gel which

will hereinafter be described was prepared and its adsorptive properties studied with an organic and an inorganic gas. Because of the fact that three chief factors influence the adsorptive activity of a gel, these three factors will be considered separately as follows:

1. Method of preparation;

2. Method of purification, or removal of by-products;

3. Method of drying and activation; and, finally, test of,

4. Adsorptive capacity of the gels with carbon tetrachloride and ammonia gases.

EXPERIMENTAL

1. PREPARATION OF GEL.

A series of silica gels was first prepared containing varying concentrations of sodium silicate and hydrochloric acid. This acid was chosen because of the ease with which alkaline chlorides diffuse from gels. This was accomplished by varying the specific gravity of the sodium silicate solution while keeping the quantity of acid used fixed. The series of gels was made with the view of choosing for the following experimental work a gel which conformed more nearly from the physical standpoint to the best gels described in the literature. A commercial water glass was used having a specific gravity of 1.3960 and with a Na_2O - SiO_2 ratio of 1 to 4.2. In the following analysis methyl orange was used as an indicator.

TABLE 1

Composition of Water Glass

Sodium oxide (Na_2O)	7.72%
Silica (SiO_2)	32.42%
Moisture	59.86%
Specific gravity	1.396

The method of preparation of these gels was similar to that used by Smits,[27] precautions being taken to be uniform in procedure. The gel finally selected was made from the following mixture:

Water glass solution (sp. gr. 1.1)	4 parts
HCl (sp. gr. 1.057)	1 part

This mixture set to a clear gel in 6 hours, from which syneresis was complete in 5 days.

A method was now developed for impregnating the gel with colloidal ferric oxide. Several methods were tried which were more or less successful, but as the final gel was unsatisfactory, these were rejected one by one. Ferric chloride solution was added directly to the water glass, but due to the hydrogen ion from hydrolysis the mixture set immediately into a coarse streaky gel. Very dilute ferric chloride was added with no better result. The pure silica gel, undried, was immersed in a solution of ferric chloride for several days, and then boiled to facilitate hydrolysis. The gel was broken into smaller pieces which were so brittle that they easily crumbled. This was repeated with the solid gel, using a concentrated solution of ferric chloride. The immersion was carried on for several days. By the color of the cross section of the gel, it was seen that the ferric chloride solution had penetrated the gel in a uniform manner. The gel was then removed from the solution and partly dried without washing. The gel was then soaked in distilled water, and after 24 hours the ferric chloride was found to have completely diffused out. This was repeated, allowing the gel to dry spontaneously for several days in an attempt to duplicate the method of Briggs.[25] The final gel became so brittle that it could not be handled readily without crumbling, while a white chalky crust formed on the outside.

A ferric oxide hydrosol was then prepared by hydrolysis of the chloride in boiling water. This was cooled and then used to dilute the water glass. A clear, transparent mixture resulted. The hydrochloric acid was then added with rapid stirring, and after a short time a clear, reddish brown gel formed. This was allowed to dry for three days and then

placed in distilled water. After soaking two weeks in running water, the gel was found to have changed color but slightly, so this method of preparation was decided upon.

A series of gels was prepared, each member of which shall be designated as C_o, C_1, C_2, C_3, etc., and each containing a small variable quantity of iron with the exception of C_o which contains no iron except a trace which was found present in the water glass. It was found that by diluting one part by volume of water glass with three parts by volume of distilled water, a mixture would be obtained which had the required specific gravity, namely, 1.10. The gels were obtained from the following mixtures:-

(C_o) Water glass.....125 cc.

Distilled water.....375 cc.

HCl (Sp. Gr. 1.057).....100 cc.

(C_1) This gel was made in the following manner:-

375 cc of distilled water was brought to boiling. Then 0.25 cc of a highly concentrated solution of ferric chloride was added drop by drop. A pure red hydrosol was obtained. This was cooled to room temperature and then added to 125 cc of the original water glass with constant stirring. This mixture was then placed in an evaporating dish and 100 cc of the dilute hydrochloric acid added with vigorous stirring across the dish. After a short time, a reddish brown gel formed.

The rest of the series was made exactly as described for (C_1) with the exception that different quantities of the concentrated ferric chloride solution was added to the different gels. Due to the formation of HCl during hydrolysis of the ferric chloride, each gel contained a larger quantity of this acid than the one before it in the series. This

had a noticeable effect on the speed of gelation, which varied from 6 hours in the case of (C_o) to 20 seconds in the case of (C_{11}). The following table will prove useful in comparing the quantity of ferric chloride solution added to speed of gelation.

TABLE 2

Gel	Volume of $FeCl_3$ solution added	Time of Gelation
C_o	None	6 hours
C_1	0.15 cc	5 hours
C_2	0.25 "	12 minutes
C_3	0.50 "	5 minutes
C_4	0.75 "	3 minutes
C_5	1.00 "	1 min. 50 sec.
C_6	1.25 "	1 min. 25 sec.
C_7	1.50 "	1 min. 10 sec.
C_8	1.75 "	1 minute
C_9	2.00 "	45 seconds
C_{10}	3.00 "	30 seconds
C_{11}	4.00 "	20 seconds

The above observations were made from the time of starting the addition of the acid to the first appearance of gelation. The acid was added as rapidly as possible, about ten seconds being taken for the addition. A stop watch was used in all cases except (C_o) and (C_1) which are but approximations. After the first appearance of gelation, it proceeded very rapidly, but a few seconds elapsing until the mixture had completely set to a gel. See figure I.

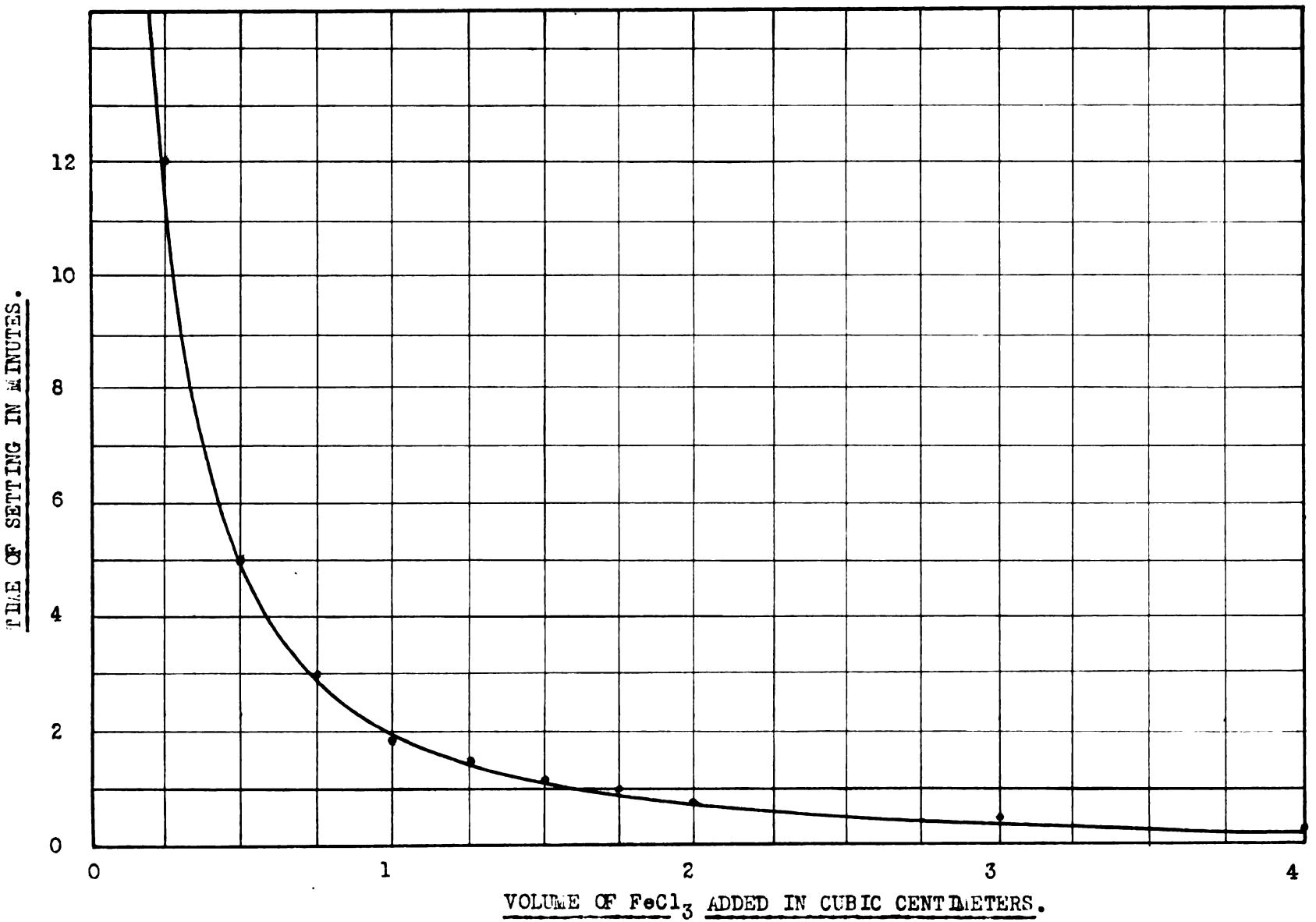
TIME OF SETTING IN MINUTES.
12
10
8
6
4
2
0
0
1
2
3
4
VOLUME OF $FeCl_3$ ADDED IN CUBIC CENTIMETERS.

Figure 1.

2. PURIFICATION OF GELS.

The gels were allowed to set in the open air at room temperature for four days, during which time syneresis was evident. At this time the gels showed an average moisture content between 45% and 55%. They were then broken into small cubes approximately one inch on each edge. These were each placed in a two liter beaker and covered with distilled water. The water was changed six times each day for two weeks, at the end of which time all evidence of chloride ion had vanished according to tests made with silver nitrate. The above method of washing was found to be more efficient than running water. The latter method was tried on several gels previous to this time, using a constant level siphon and drawing the liquid from the bottom of the container below the gel. A much longer period was found necessary for washing the gel free of chlorides than in the case of decantation, in which case ten days was sufficient, though four days longer was taken as an added precaution. Jordis[28] found, by soaking a gel of silicic acid in cold water, that the sodium salt of the acid used and the excess of acid diffused out of the gel until neither was present according to tests. If the gel is further washed in water at a temperature of 100° C, the sodium salt, from evaporation determinations, does not diminish. This led him to believe that a definite silicate was forming with the sodium and dissolving in the water.

3. METHOD OF DRYING AND ACTIVATION OF THE GELS.

After the gels had been washed for two weeks by the method of decantation, they were ready for drying. At this stage the gels had become somewhat lighter in color than originally and were found to have swelled considerably. The moisture content averaged 80%. Care was exer-

cised in handling these gels as they were more fragile, due probably to the large moisture content. Precautions were taken to prevent the larger lumps from breaking down. These gels were then ready for the first stage of drying. As the purpose of the experimental work was to produce an active gel, and as the value of silica gel as an adsorbent is due to its enormous specific surface, all precautions are necessary to prevent injuring the delicate cullular structure of the gel, which injury would diminish the surface. Any decrease in surface would affect the gel as an adsorbent.

These gels were now placed in a drying box built for this purpose, which was 3 feet long, 18 inches wide, and 12 inches deep. The bottom was removed and a double thickness of cheese cloth stretched tightly across the opening. A cheese cloth was also stretched across the top of the box to keep out the greater part of the dust. Though the gels were never exposed to a temperature higher than 35° C, they dried very rapidly. As they dried, they decreased in size and consequently became deeper in color. At the end of three days, they had decreased in volume about 30% and at the end of 5 days about 75%. The gel which contained no iron (C_o) behaved a little differently. During washing it increased but little in size, did not become fragile, and finally dried much more slowly, about seven days being necessary to dry this gel. The final product was a clear, hard gel which had a glassy fracture. It would easily scratch glass. The gels containing the iron dried down to hard, brittle gels, whose color varied from light amber to deep, reddish brown and whose moisture content varied from 13% to 18%. These gels were then ready for activation.

By activation is meant the freeing of the surface of the adsorbent of all materials not actually part of its structure. Many investigators consider water as part of the structure of silica gel.

Freundlich[16] believes that sols and gels are very similar, the difference being in the quantity of dispersion medium present. In the case of silica gel, the solid particles are separated by an adsorbed film of water. Frankenheim, Von Nageli, Bachmann, Zsigmondsy, McBain, and many others favor this view. Zsigmondy[29] by ultramicroscopic inspection found that the lower the concentration of sodium silicate used in the gel preparation, the smaller were the particles. Patrick[6] found during his experiments with silica gel and sulphur dioxide that there was a lower limit of moisture content beyond which decrease in activity occurred. Ruth,[30] working with a Patrick gel, found a decrease in activity of those gels which were activated above 250° C. For the above reasons it was decided to limit the final temperature of activation to 250° C.

The apparatus used for this work is shown in figure 2. The gel to be activated was placed in a large U tube c, which was in turn placed in an old rape seed oil bath d. The fresh rape seed oil was previously heated for 24 hours near its boiling point to drive off impurities. During this process it became dark brown and viscous. Upon cooling and reheating, it increased in temperature uniformly with no apparent vaporization. Rubber stoppers were fitted into the U tube and through these air was admitted by means of a hard glass lead-in tube. This was insulated with asbestos. The "T" was equipped with a thermometer well e. The glass lead-in tube and "T" were sealed together by tightly winding asbestos cord across the junction. A sealing compound of glycerine and litharge was poured over this cord, and then heated with a smoky flame. A partial reduction of the litharge by the glycerine occurred, and a hard, gray-colored seal was obtained. This could be easily broken by pouring hot water over the seal. The glass "T" was connected to an iron tube f

which was filled with shingle nails which acted as an air baffle. This tube was heated by gas. Connected to this tube on the opposite end was a U tube g filled with dehydrated $CaCl_2$, and to this was connected a bubbling column filled with concentrated C.P. H_2SO_4. Air was drawn through the system by a suction pump connected to a safety trap b by tube a. This trap was placed in the system as a precaution against back pressure should anything go wrong with the suction pump. After the gel to be activated was placed in U tube c, the temperature was brought up to 85° C by means of a burner placed under d. Air was drawn through the system simultaneously at the same temperature as the oil bath. The temperature was kept between 80° C and 90° C for six hours. During this time water vapor was seen to condense in b. The temperature was then raised to 250° C and kept at this point for two hours. The stop cocks were then closed, thus isolating the U tube and contents, then the system was allowed to cool. After cooling, the gel was placed in an erlenmeyer flask which was then sealed with collodion. Each gel was activated in the manner just described. The volume of air per minute drawn through by suction was kept constant by counting the bubbles per minute which passed through the H_2SO_4 column h.

After activation, the gels were found to have changed their appearance from a shiny, reddish brown to a dull, red purple.

The moisture and iron content of each gel was now determined. Each gel was pulverized by use of an agate mortar until it passed through a 40 mesh sieve. One gram samples were used for moisture determinations. These were placed in a platinum crucible and heated for exactly two minutes one inch above a meker flame. This length of time was found to be sufficient to remove all moisture. The gels were found to change from a purple-brown color to pure white during heating. Upon cooling a faint greenish tinge was evident in the gel.

The iron content of each gel was determined by the method of Zimmermann and Reinhardt, with the exception that the silica was first removed as SiF_4 by means of hydrofluoric acid. Table 3 shows the moisture content, and iron content as Fe_2O_3.

TABLE 3.

Gel	Grams H_2O per Gram of Gel	Grams Fe_2O_3 per Gram of Gel
C_0	.0421	Trace
C_1	.0647	.0023
C_2	.0753	.0049
C_3	.0717	.0059
C_4	.0662	.0071
C_5	.0542	.0087
C_6	.0489	.0097
C_7	.0531	.0106
C_8	.0566	.0118
C_9	.0650	.0128
C_{10}	.0721	.0173
C_{11}	.0864	.0226

The abnormally high moisture content of C_{11} may be accounted for by the water of hydration held by the Fe_2O_3 which is additive with the water of structure of the gel. This is undoubtedly the case with each gel with the exception of C_0 which has the lowest moisture content of the series.

4. ADSORPTION WITH CARBON TETRACHLORIDE.

Adsorption has been defined as a loose fixation of a substance at an interface.[16] This may be positive or negative, though the latter is usually so small as to be unmeasurable. Adsorption is the result of a differential existing between the rate of condensation and evaporation at an interface.[31] This is due entirely to intensity of surface forces. According to Langmuir, there are two distinct classes of adsorption, namely, chemical and physical.[31] By chemical adsorption is meant the type exhibited by active adsorbents such as metals, and by physical that shown by inert adsorbents such as mica, silica, and charcoal. He further differentiates between the two types of adsorption as primary and secondary, primary adsorption being due to primary valence forces while secondary adsorption is due to secondary valence forces. It follows that the latter is the weaker of the two forces considered. Benton[32] classifies these two types according to temperature and pressure effects, showing that secondary adsorption decreases rapidly and continuously with increasing temperature, but increases gradually with increasing pressure. Primary adsorption, on the other hand, first increases and then decreases with increasing temperature, but increases very rapidly with increasing pressure.

Ray[23] concludes from his researches that an adsorbent has a greater adsorptive capacity for those compounds which fall in the same class with respect to their origin, i.e., organic or inorganic, and will preferentially adsorb those compounds, afterwards exhibiting great retentivity when heated and evacuated.

The adsorptive capacities of this series of gels was determined dynamically. Dry air saturated with CCl_4 was passed over a weighed sample of the gel until no further increase in weight was observed.

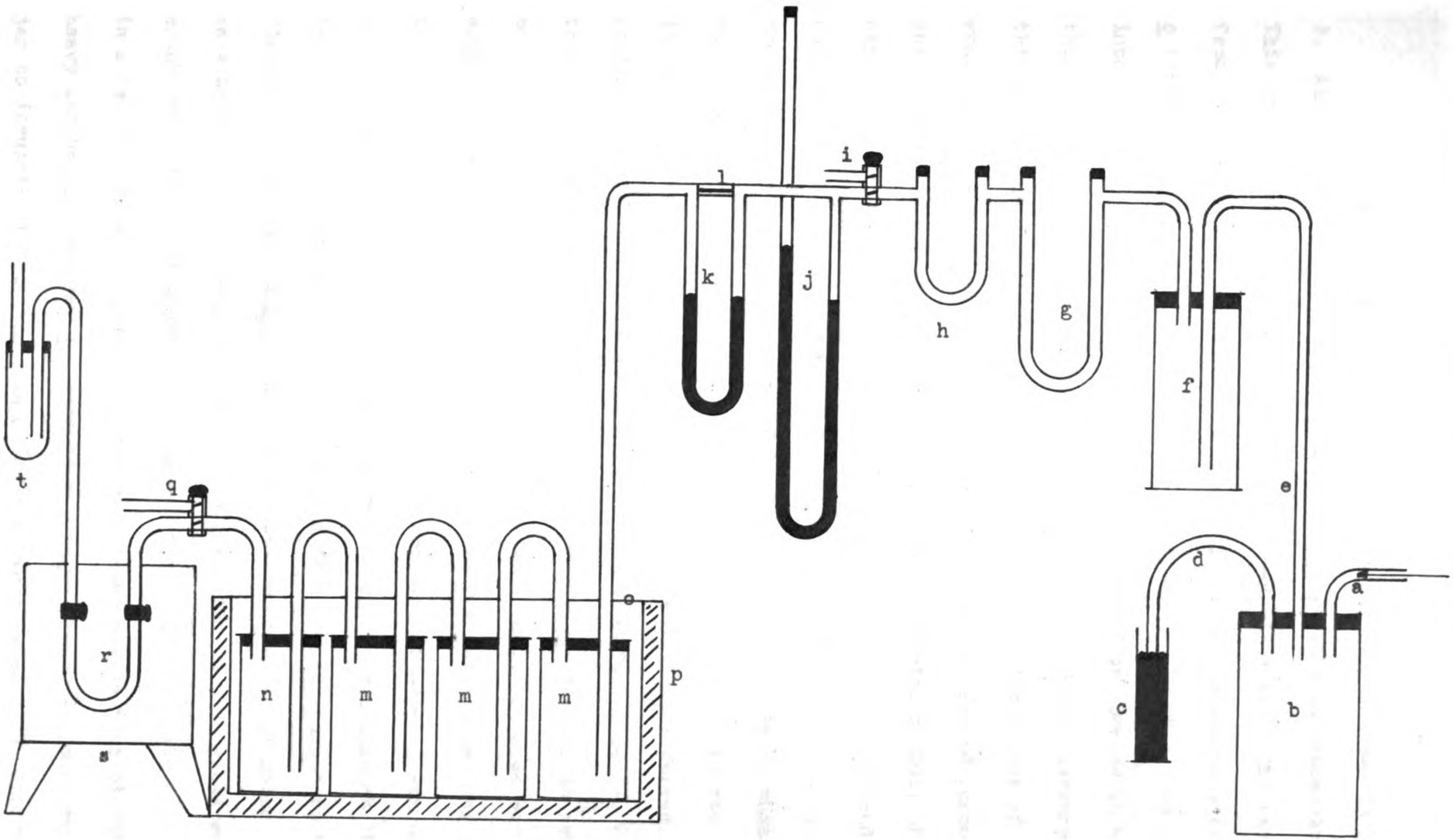

Figure 3.

The adsorption train used for this purpose is shown in figure 3. Air was pumped into chamber b which was kept at room temperature. This chamber provided a means for trapping any oil which might pass over from the blower, and likewise to connect the system to a safety column c through tube d. This safety column consisted simply of a tube dipping into a mercury column. The column could be raised or lowered at will, thus increasing or decreasing the height of the column of mercury. In this manner any desired pressure could be obtained, the excess of which would be relieved through the safety column. The air passed through e into a bubbling column f which was filled about two-thirds full of concentrated C.P. H_2SO_4. This column served both as an air dryer and a means for checking the manner in which the pump was functioning. Any leak in the system beyond this point could be detected by the rate at which the air bubbled through the column. From the column f the air passed to a large U tube which was filled with dehydrated $CaCl_2$. This served as an additional dryer and likewise as a spray trap from f. In series with this U tube was a smaller U tube h filled with glass wool which screened out any dust particles which might be carried from g. A three way stopcock i was placed in the system at this point for safety purposes should the blower fail to function properly. A mercury barometer j was used to measure the pressure in the system before the air passed through the capillary l of the flowmeter k. From the flowmeter the air passed to three flasks m filled with CCl_4. These also contained glass wool which served as a baffle for the air. A fourth flask n was filled with glass wool to catch any spray which might pass from the CCl_4. These flasks were placed in a large rectangular glass battery jar o which was in turn placed in a heavy cardboard container p. Sawdust was tightly packed around the glass jar to insulate it from the room. Ice was packed around the saturation

train in the glass jar, and the train covered. The air passed from the saturation train into a U tube r which contained a known weight of activated gel. The U tube was placed in a constant temperature Weber electric furnace s and the temperature regulated to 35° C. Tube t contained H_2SO_4 through which the air was discharged. This acted both as a seal and a means for detecting any leak in the system between stop-cock i and tube t. The adsorption was carried on as follows:

Each gel was ground in an agate mortar until it passed through a forty mesh sieve. It was found in each case that 23% to 25% of the total gel would not pass through a sixty mesh sieve, 10% to 12% would not pass through an eighty mesh sieve, 20% to 25% would not pass through a one hundred mesh sieve. The remainder passed a one hundred mesh sieve.

A sample of the gel was placed in U tube r which had previously been weighed. The tube and gel was reweighed and then placed in the furnace and connected in series with the train. The gel was allowed to stay in the furnace for 30 minutes to arrive at the same temperature as the furnace. The stop-cock q was now opened to the air and the blower started. The pressure was adjusted until a differential of 5½ centimeters was obtained across the flowmeter. Safety column o was then adjusted until air just started to bubble through the column. The pressure was then readjusted until a differential of 5 centimeters was observed across the flowmeter. The stop-cocks of U tube r were then opened, and finally stop-cock q was closed to the air and opened to the system. At intervals of 15 minutes the gel was reweighed until a constant weight was obtained over one-half hour. At the above pressure differential 100 cc. of gas per minute passed through the gel.

The adsorption capacity of the different gels toward NH_3 was now tested. The gas was passed directly through the flowmeter into the

weighed gel which had previously reached the temperature of the furnace. A pressure differential of 5 cm. was used as before. Table 4 shows the results of the adsorption tests.

TABLE 4

Gel	Grams CCl_4 ads. per gram of gel	Grams NH_3 ads. per gram of gel	Grams H_2O + grams CCl_4
C_0	.0454	.0387	.0875
C_1	.0299	.0265	.0946
C_2	.0206	.0204	.0959
C_3	.0297	.0300	.1014
C_4	.0376	.0359	.1038
C_5	.0488	.0440	.1020
C_6	.0509	.0385	.0998
C_7	.0468	.0330	.0999
C_8	.0402	.0305	.0968
C_9	.0381	.0280	.1031
C_{10}	.0279	.0232	.1000
C_{11}	.0238	.0215	.1102

The curves shown in figure 4 furnish a means for comparing the weight of CCl_4 adsorbed by one gram of the different gels during equal intervals of time at 35° C. They take the form of saturation curves, and show the adsorption rate of the various gels.

DISCUSSION

From Figure 1 and Table 2 it is seen that the relative time of gelation for the different gels varies with the quantity of ferric chloride added. Ferric chloride in contact with boiling water hydrolyzes very rapidly, furnishing HCl and ferric hydroxide according to the following equation:

$$FeCl_3 + 3\ H_2O = Fe(OH)_3 + 3\ HCl$$

It is believed that $Fe(OH)_3$ exists as a hydrated oxide $Fe_2O_3.3H_2O$, though Milligan[33] claims that no definite hydrated oxide of iron exists.

It is seen that the speed of gelation changes enormously between gels C_o and C_{11}. This is surprising when the relatively small increase of hydrogen ion over the original hydrogen ion concentration is considered.

The increased speed of gelation of the gels with increase in ferric chloride is of interest. Following is the increase of speed of gelation over the previous one in the series, with the ascending series of ferric chloride concentration:

C_o - 1, C_1 - 1.33, C_2 - 25, C_3 - 2.4, C_4 - 1.7, C_5 - 1.64, C_6 - 1.3, C_7 - 1.21, C_8 - 1.17, C_9 - 1.33, C_{10} - 1.67, C_{11} - 1.67.

The total increase in gelation speed from C_o to C_{11} is 1080 times.

Figure 4 is a graphic representation of the relative speed of adsorption of the different gels at a definite temperature. These are typical saturation curves. The following table indicates the increase in weight of the gels due to adsorption of the CCl_4 at definite intervals of time.

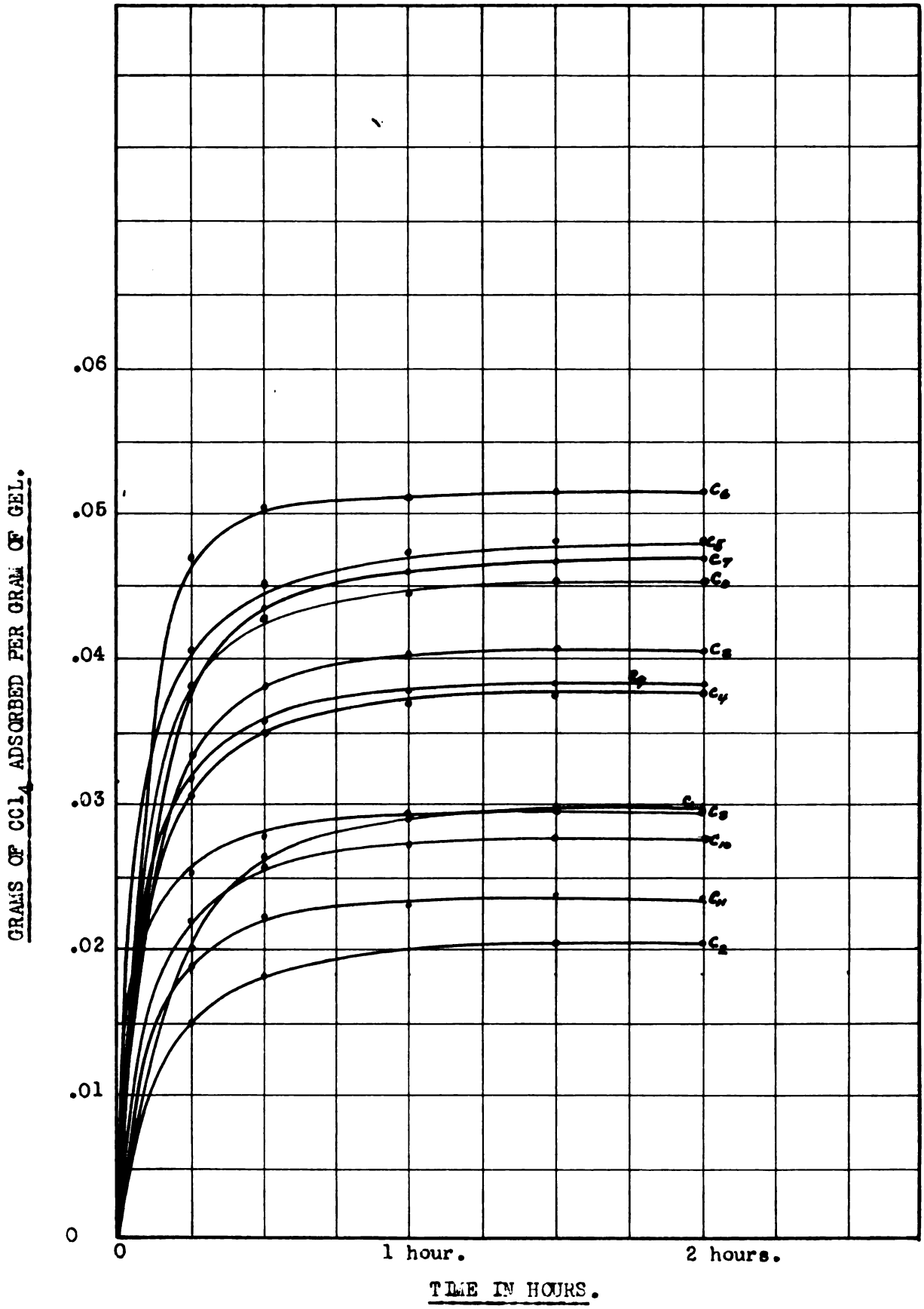

Figure 4. (Temp. 35° C.)

TABLE 5

Gel	15 min.	15 min.	½ hr.	½ hr.	½ hr.	Total ads. per gram of gel
C_0	.0380	.0050	.0019	.0005	0000	.0454
C_1	.0255	.0025	.0015	.0004	0000	.0299
C_2	.0150	.0034	-----	.0022	0000	.0206
C_3	.0200	.0055	.0035	.0007	0000	.0297
C_4	.0310	.0040	.0030	.0006	0000	.0376
C_5	.0404	.0051	.0027	.0006	0000	.0488
C_6	.0470	.0034	.0003	.0002	0000	.0509
C_7	.0380	.0060	.0020	.0008	0000	.0468
C_8	.0340	.0040	.0022	-----	0000	.0402
C_9	.0320	.0040	.0015	.0006	0000	.0381
C_{10}	.0220	.0044	.0011	.0004	0000	.0279
C_{11}	.0190	.0031	.0005	.002	0000	.0238

It is of interest to note that on the average the gels adsorb approximately 81% of the total amount in the first 15 minutes.

Specific adsorption of the different gels with CCl_4 and NH_3 was plotted. These are shown in figure 5. The gels are represented on the abcissa by their Fe_2O_3 concentrations. With CCl_4 it was found with the ascending concentrations of Fe_2O_3 the curve reached a minimum for C_2 (see table 3). With increasing Fe_2O_3 concentration specific adsorption increased until gel C_6 was reached, and then slowly decreased to the end of the series. The NH_3 curve is very similar with the exception that maximum specific adsorption occurs with gel C_5. The moisture content of the gels with the ascending Fe_2O_3 concentrations

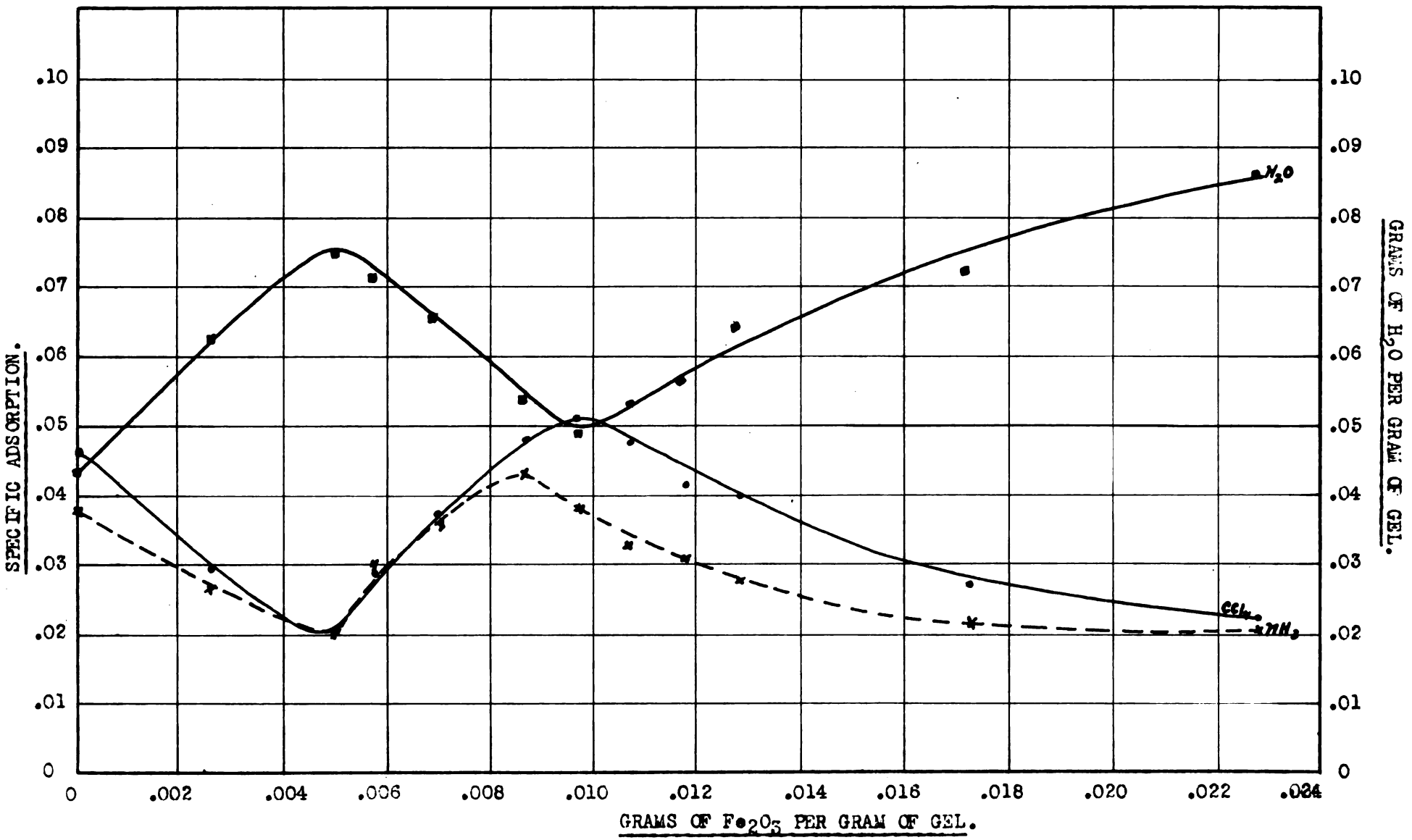
SPECIFIC ADSORPTION.
GRAMS OF H_2O PER GRAM OF GEL.
GRAMS OF Fe_2O_3 PER GRAM OF GEL.
H_2O
CCl_4
NH_3
0
.01
.02
.03
.04
.05
.06
.07
.08
.09
.10
.002
.004
.006
.008
.010
.012
.014
.016
.018
.020
.022
.024

Figure 5.

was also plotted on the same graph with the same scale. It is seen that the water content reaches a maximum for gel C_2 and a minimum for gel C_6. Gel C_0 likewise appears as a minimum. As the Fe_2O_3 concentrations increase from C_6, the moisture content gradually increases. When the CCl_4 and moisture curves are observed together, a marked relationship is readily observed. The moisture curve appears to be a mirror image of the CCl_4 curve, i.e., a minimum exhibited by the CCl_4 corresponds to a maximum on the moisture curve. Where the slope of the CCl_4 curve is positive, the slope of the moisture curve is negative, and vice versa.

From the manner of behavior of silica gel when heated, it appears that the view of Freundlich[16], Patrick[6][7][8], and others regarding the structure is correct. It is probable that the particles which make up the gel are of the same size as those which make up the sol. In the case of gelation, the continuous phase has decreased greatly in volume and the colloidal particles are more closely packed. Slow drying allows these particles to pack themselves in a normal manner with a maximum number of pores of uniform size. The colloid particles (SiO_2) are surrounded by a film of water which allows limited motion to the mass. This film of water, which constitutes the continuous phase, preserves the gel structure and consequently preserves the number and size of pores. The number of pores undoubtedly does not change during preliminary drying and activation, though it is very probable that their size does change. As the moisture escapes, the particles settle together, thus decreasing the volume of the inter-space and consequently the pore size. These interspaces between particles constitute the pores. After activation, it is believed that the remaining water is adsorbed on the particles. If this is removed by heating, the moisture is replaced by air bubbles which give

a chalky appearance to the gel. Upon still further heating, these air bubbles disappear and the pores become uniformly filled with air. The gel then becomes glassy, transparent again. Any remaining water is strongly adsorbed and the gel irreversible and inactive at this point. It was believed that if it were possible to uniformly fill these pores with colloidal particles of very small dimension, such as Fe_2O_3, the number of pores would be increased and a still greater surface would be presented. Together with this it was believed that Fe_2O_3 would exhibit a powerful adsorption for gases which would penetrate into the pores.

It will be recalled that during activation of these gels a change in color from reddish brown to purplish was observed as the moisture content decreased. When further heated -- during moisture content determinations -- the gels became pure white. Upon cooling, a yellowish green tint was observed, which was due to the iron present, probably as a mixture of ferrous and ferric silicate. Upon addition of water no change took place, which showed the change to be irreversible. The change from red-brown to purple-brown during activation was undoubtedly due to a change of water of hydration, a different hydrate being formed.

Due to the increasing Fe_2O_3 content of the gel series, they were expected to show brittleness after activation in direct proportion to their iron concentration. This was expected on the basis of the outcome of Fells and Firth's[34] researches. This brittleness did not materialize, however. The fact that the gels were highly colored after activation was sufficient to indicate the colloidal nature of the Fe_2O_3 present, at least to some extent. Undoubtedly some agglomeration had taken place during the gel contraction, which may have resulted in the formation of a different hydrate, thus changing the color of the gel.

From figure 5 it is seen that maximum adsorption occurs at minimum moisture content, and minimum adsorption at maximum moisture content. If the weight of water per gram of gel be added to the weight of CCl_4 adsorbed per gram of gel (see table 4), it is seen that the sums are nearly constant. The average of these sums is practically identical with the sum obtained from C_6. This leads to the opinion that the iron content had nothing whatever to do with the activity of the gel. The moisture content does, however. This may be explained by assuming a maximum adsorption capacity of the original silica gel (C_o). By varying the water content of water by hydration of Fe_2O_3, and water of structure, part of the adsorption capacity was satisfied. Upon addition of CCl_4 the remaining capacity was satisfied, and the series of gels exhibit varying degrees of adsorptive capacity due entirely to the difference in moisture content.

The NH_3 curve is very similar to the CCl_4 curve, though from the researches of Patrick and Davidheiser[8] it was expected that the adsorptive capacity of the gel would vary directly with the moisture content. The results do not show this, however, which is an indication that the total water present is not free to take up the NH_3.

CONCLUSIONS

1. Colloidal hydrated ferric oxide was highly protected by the sodium silicate when the acid was added. This was evidenced by the characteristic red color of the gel after setting. Upon washing this gel, the color remained.

2. During activation, the red-brown color of the gel changed to red-purple. This was due to loss of water of hydration of the ferric oxide, a different hydrated oxide being formed.

3. The specific adsorption curves for both CCl_4 and NH_3 showed maximum adsorption with minimum moisture content, and minimum adsorption with maximum moisture content. The adsorptive capacities of the gels therefore vary inversely with their moisture content.

4. The specific adsorption curves show maxima and minima regardless of the iron concentration of the gel. The iron content therefore has no effect on the adsorptive capacity of the gel.

5. The structural water of the gel and the total water are not the same, nor do they exhibit the same effects on adsorption. This is shown by the behavior of NH_3 with C_0 in contrast with the rest of the series. According to Patrick and Davidheiser, the adsorptive capacity for NH_3 should vary directly with moisture content. This is not true for the series of gels used in these experiments.

6. The water held by the Fe_2O_3 is water of hydration and does not give the same effect as the water of structure of the gels.

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