

THE ADSORPTIVE CAPACITY OF SILICAS  
FOR BENZENE VAPOR

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Research in the preparation of activated silicic acid gel has been in two fields: first, in the reagents used for the preparation of the gel, and second, in the physical or mechanical features of its preparation. Activated silicic acid gels have been prepared from the following reagents: sodium silicate and hydrochloric acid (1), nitric acid (2), sulfuric acid (3), carbon dioxide (4), sulfur dioxide (4), chlorine (5), ferric chloride (6), copper sulfate (6, 7, 8), aluminum chloride (6), aluminum sulfate (6), chromium sulfate (6), and also by hydrolysis of silicon halides or sulfide (9, 10).

Holmes and his associates (6, 7) found that when a gel was placed in a stoppered bottle it tended to exude water, and that such a gel upon being washed free from impurities, dried and activated possessed a higher adsorptive capacity than gels not similarly treated; and, that the adsorptive capacity of a gel could be increased by boiling with 6N to 9N sulfuric acid (the so-called "wet heat treatment gel"). It was also pointed out by Holmes that the presence of tri-valent ferric ions had a strong precipitating effect upon the colloidal silicic acid always present in a solution of sodium silicate.

Holmes and his associates also found that if calcium chloride, cupric chloride, chromium chloride, or aluminum chloride were used in place of ferric chloride in the preparation of silicic acid gel the results were less satisfactory. The explanation given was that there is an optimum sized capillary for each gas or vapor and that the gels produced by use of calcium chloride, etc., did not approach the optimum. According to Bancroft (11) the state of subdivision and the proper regulation of the peptizing agent could also aid in accounting for this.

Recently I. G. Farben Industrie, Ger. 530,730, prepared an activated gel from water glass and gaseous carbon dioxide and sulfur dioxide. This method is unique in that the sodium silicate and silicic acid mixture undergoes gentle constant stirring as the gas bubbles through.

M. O. Kharmandaryan and S. L. Kappellevich (12) have prepared activated silica gel from sodium silicate using hydrochloric acid, sulfuric acid, ferric chloride, and aluminum chloride. They found that a slight excess of acid above the neutralization point greatly reduced the adsorbing power of the gel for benzene vapor. The speed of introduction of acid and cessation of stirring after gelation do not affect the activity of the gel. The gel obtained by precipitation with the minimum quantity of acid produced the lowest yield of gel possessing the maximum activity.

The object of this investigation was to compare the adsorptive capacities of various activated silicas for benzene vapor.

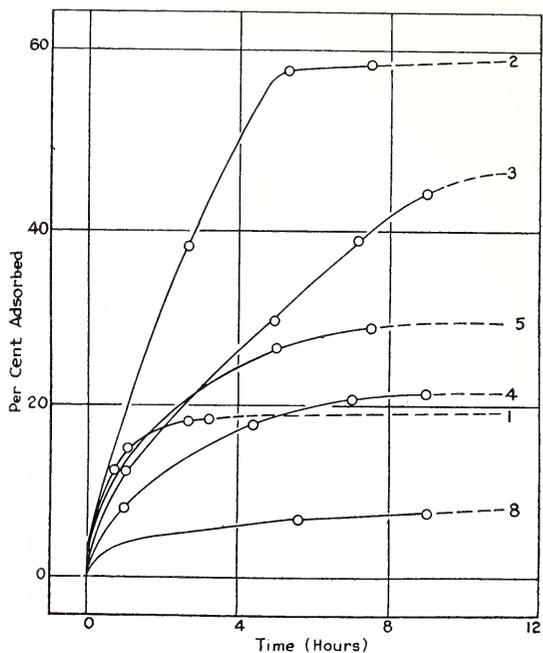


Fig. 1

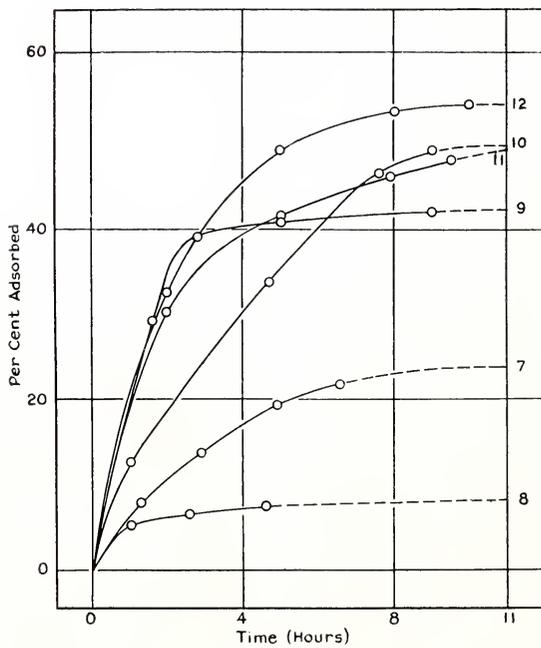


Fig. 2

## EXPERIMENTAL

**Materials:** The sodium silicate, commercial quality, sp. gr. 1.38, was obtained from Mallinckrodt Chemical Company. The ferric chloride, copper sulfate and aluminum sulfate were of C. P. quality from J. T. Baker Company. A sample of silica gel (Table 1, gel 24) was obtained from the Silica Gel Corporation of Baltimore, Maryland (Grade  $\frac{1}{2}$ , No. 150-G-600-1420).

**Preparation of Gels:** The activated silica gels were prepared according to the methods outlined in Table 1. The gels were precipitated from solutions of sodium silicate of the indicated sp. gr. by the addition of the particular precipitating agent. The stirring method and time of stirring is indicated in the table. After precipitation the gels were filtered and washed in a Buchner funnel on a cloth or paper filter. The gels were then spread out on a cloth supported by  $\frac{1}{4}$ -inch mesh galvanized screen for a definite period of time. Some gels were allowed to sweat by placing in a closed glass vessel at room temperature for a period of days. Other gels were placed directly in an oven at  $100^{\circ}$  C. for drying. After drying, gels numbers 1-19 inclusive were activated for four hours at  $450^{\circ}$  C. while numbers 20-23 inclusive were activated four hours at  $250^{\circ}$  C. After activation, the gels were allowed to stand over night in a desiccator. The following day their adsorptive capacities for benzene vapor were determined by passing a stream of air saturated with benzene vapor at  $25^{\circ}$  C. over a weighed portion of the gel according to the method outlined by Holmes (13).

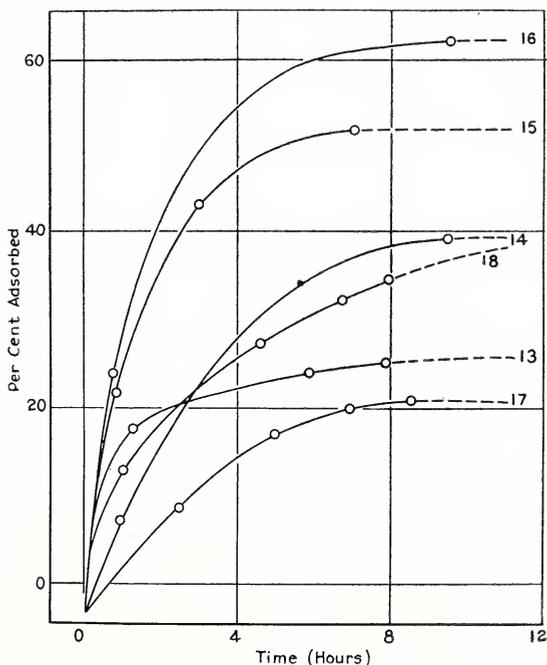


Fig. 3

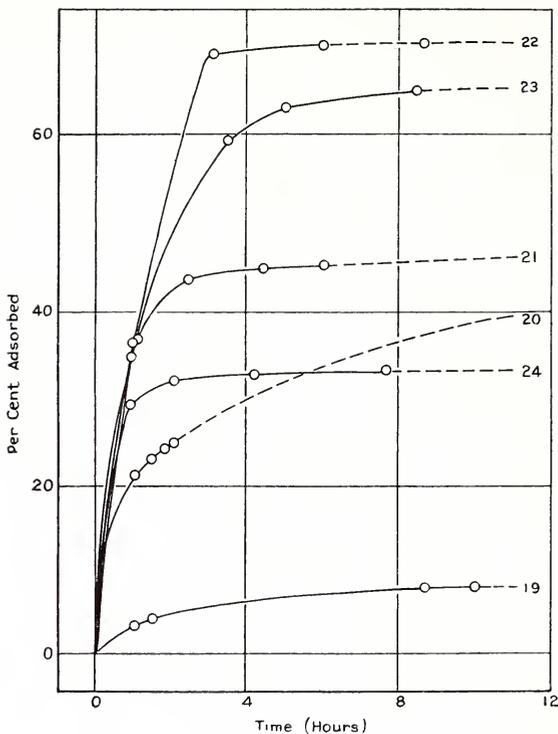


Fig. 4

Gel 1 was stirred by means of bubbling carbon dioxide for ten minutes at fifteen-minute intervals until gelation started, and then was allowed to stand until complete gelation occurred. Gel 2 was stirred in the same manner as 1 except that the stirring was continued beyond the point of gelation as long as mechanically possible. Gel 8 was stirred mechanically for thirty seconds at intervals of three minutes.

Gel 20 was prepared in the same manner as Holmes' wet heat treatment gel up to the point where it was to be given the wet heat treatment, at which time it was washed with hot water until free of chlorides. The ferric oxide was removed by washing with 5 per cent hot sulphuric acid solution and then with hot water until free from sulphates. Gel 21 was given the Holmes wet heat treatment (13).

In the preparation of certain gels pectizing agents were added: gel 22, 100 cc. of 30 per cent ferric chloride solution, and gel. 23, 100 cc. of 30 per cent copper sulfate solution. In preparing these gels the amount of pectizing agent was regulated by first adding a given amount of acid and then adding slowly with constant shaking the given amount of pectizing agent whereupon precipitation occurred.

**Data:** The last column of Table 1 shows the per cent of benzene vapor adsorbed by the various silica gels. Figs. 1-4 inclusive show the curves obtained when the per cent of benzene vapor adsorbed is plotted

against the time in hours that the gels were exposed to the air saturated with benzene vapor (25° C.). From these curves a comparison of the rates of adsorption can be made.

TABLE 1

No. of Gel.	Sp. gr. Na <sub>2</sub> SiO <sub>3</sub> Sol.	Gms. of Na <sub>2</sub> SiO <sub>3</sub> Sol.	Pptng. Agent <sup>1</sup>	Stirring Method	Minutes Stirred <sup>2</sup>	Ce. of Pptng. Agt. Added	Filter Used	Time on Screen in Days	Sweating Days	Hrs. Dried 100° Oven	Per Cent Benzene Vapor Absorbed
1	1.06	970.8	CO <sub>2</sub>	CO <sub>2</sub> gas	42	.....	cloth	2.58	2.5	48	18.22
2	1.06	1078.0	SO <sub>2</sub>	SO <sub>2</sub> gas	17	.....	cloth	2.58	2.6	48	58.27
3	1.06	1657.0	HNO <sub>3</sub>	air	52	40.2	cloth	2.0	2.08	48	43.49
4	1.06	1176.0	HNO <sub>3</sub>	air	49	28.4	cloth	2.0	2.08	48	22.50
5	1.06	1060.0	HNO <sub>3</sub>	air	20	28.4	cloth	2.0	.....	24	29.26
6	1.06	1060.0	HNO <sub>3</sub>	.....	.....	28.4	cloth	2.0	.....	24	8.96
7	1.06	1060.0	HNO <sub>3</sub>	meeh	30	28.4	cloth	2.0	2.05	36	21.24
8	1.06	1060.0	HNO <sub>3</sub>	meeh	30	28.4	cloth	2.0	2.5	36	7.77
9	1.06	1060.0	H <sub>2</sub> SO <sub>4</sub>	.....	.....	29.0	paper	2.0	2.0	24	77.8
10	1.06	1060.0	H <sub>2</sub> SO <sub>4</sub>	.....	.....	29.0	paper	2.0	.....	24	47.76
11	1.06	1060.0	H <sub>2</sub> SO <sub>4</sub>	meeh	20	29.0	paper	2.0	.....	24	42.72
12	1.06	1088.5	HCl	air	17	18.4	cloth	2.0	2.08	48	54.39
13	1.06	1285.7	HCl	.....	.....	21.6	cloth	2.0	2.08	48	25.11
14	1.06	1060.0	HCl	air	25	45.6	paper	1.0	2.0	24	39.53
15	1.06	1060.0	HCl	air	25	45.6	paper	1.0	2.0 <sup>3</sup>	24	52.04
16	1.06	1060.0	HCl	air	25	45.6	paper	1.0	2.0 <sup>4</sup>	24	62.75
17	1.06	1060.0	HCl	meeh	20	45.6	paper	1.0	.....	24	20.89
18	1.06	1060.0	HCl	meeh	20	45.6	paper	1.0	2.0	24	35.74
19	1.06	1060.0	H <sub>2</sub> SO <sub>4</sub>	meeh	35	29.0	paper	1.0	.....	24	8.65
20	1.019	1274.0	FeCl <sub>3</sub>	shaken	2	4000 <sup>5</sup>	paper	7.0	7.0	48	27.84
21 <sup>6</sup>	1.019	1274.0	FeCl <sub>3</sub>	shaken	2	4000 <sup>5</sup>	paper	7.0	7.0	36	50.45
22	1.016	5080.0	HCl	shaken	2	15.0	paper	4.0	6.0	36	74.05
23	1.016	5080.0	H <sub>2</sub> SO <sub>4</sub>	shaken	2	15.0	paper	3.0	6.0	36	66.55
24	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	31.55

<sup>1</sup>The acids used were concentrated and of C.P. quality. The sulfuric acid was prepared by adding 856 cc. of conc. H<sub>2</sub>SO<sub>4</sub> to 1000 cc. H<sub>2</sub>O.

<sup>2</sup>When stirring was accomplished by bubbling of gas or air, the rate of gas flow was held at 7 liters per hour.

<sup>3</sup>Gel number 15 was sweat under a pressure of 15 pounds per sq. in. The pressure was obtained from compressed carbon dioxide.

<sup>4</sup>Gel number 16 was sweat at 50° C.

<sup>5</sup>The ferric chloride solution was 2N.

<sup>6</sup>Gels numbers 21-23 inclusive were given the wet heat treatment.

## RESULTS

A comparison of gels 1 and 2, Table 1, shows that a gel prepared from sulfur dioxide and sodium silicate has an adsorptive capacity greater than one made from carbon dioxide and sodium silicate. Gel 2, however, was stirred beyond the point at which gelation occurred, which may account for some of this difference.

In general, the use of paper as a filter was superior to the use of cloth, which is probably due to the fact that more colloidal silicic acid is retained.

The use of nitric acid as precipitating agent produced gels of lower adsorptive capacity for benzene vapor than either sulfuric or hydrochloric acid.

A comparison of gel 9 with 10 and 17 with 18 shows that sweating is important in increasing the adsorptive capacity of gels from benzene vapor.

Gel 5, which was prepared in a manner analogous to 6, except that during the addition of nitric acid it was stirred by means of a current

of air bubbling through the solution, had a much higher adsorptive capacity than gel 6. This indicates that air stirring is an important factor in increasing the adsorptive capacity of these silica gels for benzene vapor. Mechanical stirring seems to cause a slight decrease in the adsorptive capacity if gel 11 is compared with gel 10. Intermittent mechanical stirring (gel 8) is a disadvantage over continuous stirring (gel 7) in the production of a highly active gel.

A comparison of gels 14, 15 and 16 shows that it is advantageous to sweat gels at a pressure of 15 pounds per sq. in. and also to sweat the gels at an elevated temperature (50° C.). It was noted that as soon as gel 15 was subjected to a pressure of 15 pounds per sq. in. at room temperature it began to sweat, which seemed to indicate that sweating was due to vapor pressure within the containing vessel. Gel 16 was sweat at 50° C. in a closed vessel at atmospheric pressure and gel 14 was sweat at room temperature in a closed vessel at atmospheric pressure. It can be concluded that sweating at an elevated temperature, consequently higher vapor pressure, is more desirable than sweating at room temperature.

A possible explanation of the increased adsorptive capacity due to sweating is that increased pressure causes increased coagulation of the colloidal silicic acid, thus preventing its loss during washing. The growth of new filaments between the older and larger filaments will increase the amount of surface exposed and thus increase the adsorptive capacity of the gel.

According to Bancroft (11) a plane surface will adsorb a certain amount of gas under standard conditions, but two plane surfaces placed close together will apparently adsorb more gas than the same surfaces would if each did not reinforce the other and modify the concentration gradient. Perhaps the fact that the adsorptive capacity of a gel increases when it is sweat or subjected to pressure is due to the forcing of the filaments closer together by vapor pressure or applied pressure. This seems to confirm in part Holmes' (14) statement, "Surely there must be a rearrangement of gel particles during this ageing to yield the firmest gel structure."

A comparison of gels 12 and 14 indicates that the addition of an excessive amount of hydrochloric acid (gel 14) decreases the adsorptive capacity. This supports the claim of M. O. Kharmandaryan and S. L. Kappellevich (12) that a slight excess of acid above the neutralization point reduces the activity of the gel.

A comparison of gel 20 with 21 shows the advantage of the wet heat treatment.

A better adjustment of the pectizing agent appears to aid in the preparation of a more active gel. This can be seen from a comparison of gel 21 with 22. To the latter was added hydrochloric acid in addition to the ferric chloride in order to modify the action of the pectizing agent.

Methods of preparation of activated silicas outlined above result in the production of many gels more highly active for the adsorption of benzene vapor than the sample of silica (gel 24) obtained from the Silica Gel Corporation.

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CATALYTIC OXIDATION OF THE CARBOHYDRATES  
AND RELATED COMPOUNDS BY OXYGEN  
IN THE PRESENCE OF IRON  
PYROPHOSPHATES

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III. Ethyl Alcohol, Acetaldehyde, Acetic Acid, and  
Sodium Acetate

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Since ethyl alcohol, acetaldehyde, and acetic acid all represent products of carbohydrate degradation under certain specific conditions, it was thought advisable to determine the stability of these compounds under the conditions of this series of experiments (1). The amounts of these substances indicated in the table were subjected to the action of oxygen in the presence of iron pyrophosphate solution at a temperature of 50° C. for a period of one to sixteen days.

In each set of experiments four control tubes were used, and the average change in weight of the control tubes was used as a correction factor. Hence the values given in the tables represent the average net change in the weight of the experimental tubes. In general, the procedure was the same as that reported in the previous papers (1 and 2).

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