STUDIES IN ADSORPTION ON GELS.

II. A Comparative Study of the Capillary Spaces in Gels of Silica and Alumina.

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The method of preparation of silica gel is known to affect the nature of the capillaries in the adsorbent. The chalky gel prepared by Holmes is known to contain much wider capillaries than the glassy variety obtained by Patrick. The total capillary volume in the former is nearly double that in the latter.[5] As has been stated in Part I of "Studies in adsorption on gels"[13] the temperature of activation of alumina gel affects its capillary space. A comparative study of the capillary volume of alumina gel activated at different temperatures was made with the aid of the McBain-Bakr quartz spring microbalance.

Experimental.

Construction of springs of quartz fibre.—The preparation of a spring of quartz fibre and its use in adsorption experiments have been studied by McBain and his co-workers.[6,7,8,9] They have employed a carbon rod for winding the spring. Cameron,[2] however, has employed a silica tube. It was found in this laboratory that better springs could be obtained when a silica tube is used. With a carbon rod the flame employed in bending the fibre, oxidises the carbon and gives the rod a rugged surface. Owing to the greater heat conductivity of carbon, the heat of the flame does not get properly localised. This results in poor bending of the fibre. To overcome this defect Pidgeon[11] has used a fluted carbon rod with longitudinal grooves. When a silica tube is employed the heat of the flame can be localised and a winding of the fibre quite close to the tube secured. Corners in the spring may thus be avoided.

The production of springs having equidistant coils is a matter of some difficulty. Such springs have been prepared in this laboratory with the aid of an automatic winding device.[3] In the absence of an automatic device satisfactory springs can be obtained if the tube employed has on its surface, a helical impression. This is obtained by rotating the rod in a lathe while the sharp edge of a glass-cutting knife is directed against the tube. In contact with the flame the scratch appears brighter than the silica surface and the helical impression can therefore be easily traced while winding.

A conical shaped bucket of thin gold sheet attached to the spring by means of silica fibres, was employed for holding the adsorbent. When dealing with fine powders it was found necessary to cover the bucket with a lid of thin gold sheet.

Thermostat.—To maintain the adsorbent at a constant temperature an air thermostat was used as shown in Fig. 1. Efficient circulation of heated

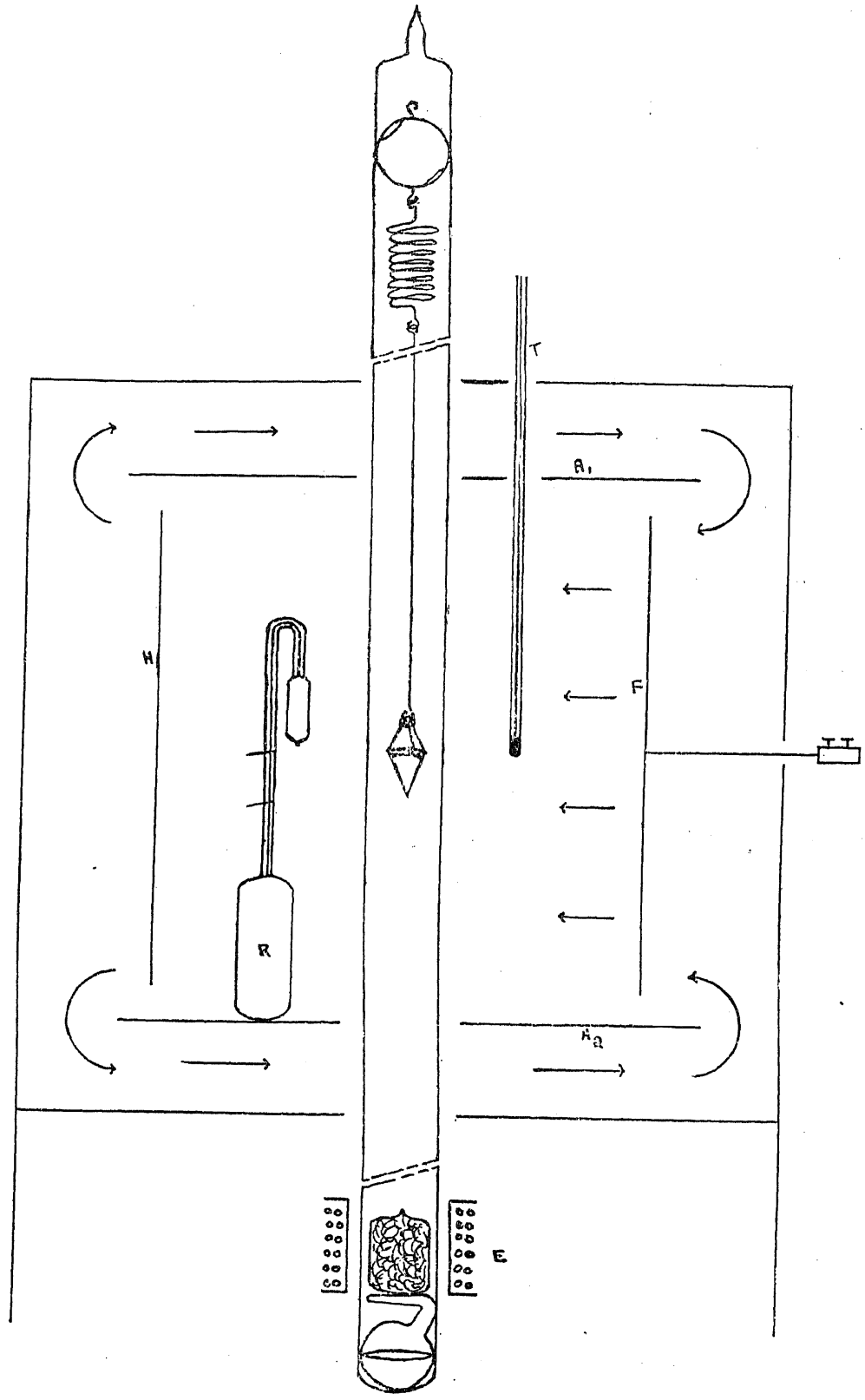

FIG. 1.

air was secured by employing the fan F. The heater H was made of heating mats. The thermo-regulator R contained mercury in vacuum in order to avoid fouling and had a temperature adjustment similar to that in a Beckmann thermometer.

The lower portion of the sorption tube containing the liquid was enclosed in a water thermostat. The thermostatic device described by Fox and Mankodi[4] was employed when the liquid had to be maintained at a temperature lower than that of the laboratory.

A Cenco travelling microscope reading correct to 0·001 cm. was used to measure the stretch of the spring during adsorption.

Materials.—Two varieties of silica gel were employed. The "glassy" variety was obtained by the method described by B. S. Rao and K. S. G. Doss.[12] The chalky gel was prepared by adding 220 c.c. of 2 N nickel chloride, to 2,000 c.c. of potassium silicate (Density, 1·02) the latter being stirred vigorously. The precipitate was allowed to settle, separated, washed with dilute hydrochloric acid in the beginning and with distilled water subsequently and the gel dried. The opaque gel was powdered and particles 1 to 2 mm. in diameter were used.

Alumina gel employed had been prepared by the method described in Part I.[13]

Pyridine.—Merck's "extra pure" pyridine was treated with solid potassium hydroxide and distilled.

Procedure.—Glass bulbs of 1·5 c.c. to 2 c.c. capacity were filled with the liquid according to the procedure described by McBain and co-workers.[10]

The bulb containing the liquid was placed in a glass tube (3′ long, 1″ diameter) as shown in Fig. 1.

The gel was activated *in situ* by heating for 6 hours at 450° C. in an electric furnace, the tube being evacuated by the mercury vapour pump backed by the Cenco "Hyvac" pump. After activation of the gel the sorption tube was sealed off from the pump. The stretch of the spring for the activated gel was then measured.

The sorption tube was next introduced into the thermostat the travelling microscope focussed to the hook of the spring. The lower end of the sorption tube was cooled in a mixture of solid carbon dioxide and alcohol. Such cooling is necessary to prevent the sudden rush of vapour into the adsorption chambers as this throws the bucket off the spring. After cooling

for half an hour, the bulb containing the liquid was broken open, by employing an electro-magnetic device (E). The thermostatic bath was then kept in position to keep the bulb at the required temperature. The course of adsorption was studied by measuring the stretch of the spring at frequent intervals with the aid of the travelling microscope.

A corresponding pressure of 0·53 was maintained. To secure this, water had to be kept at 28°·5 C. and pyridine at 27°·7 C.

Results are given in Tables I to V and shown in Figs. 2 and 3.

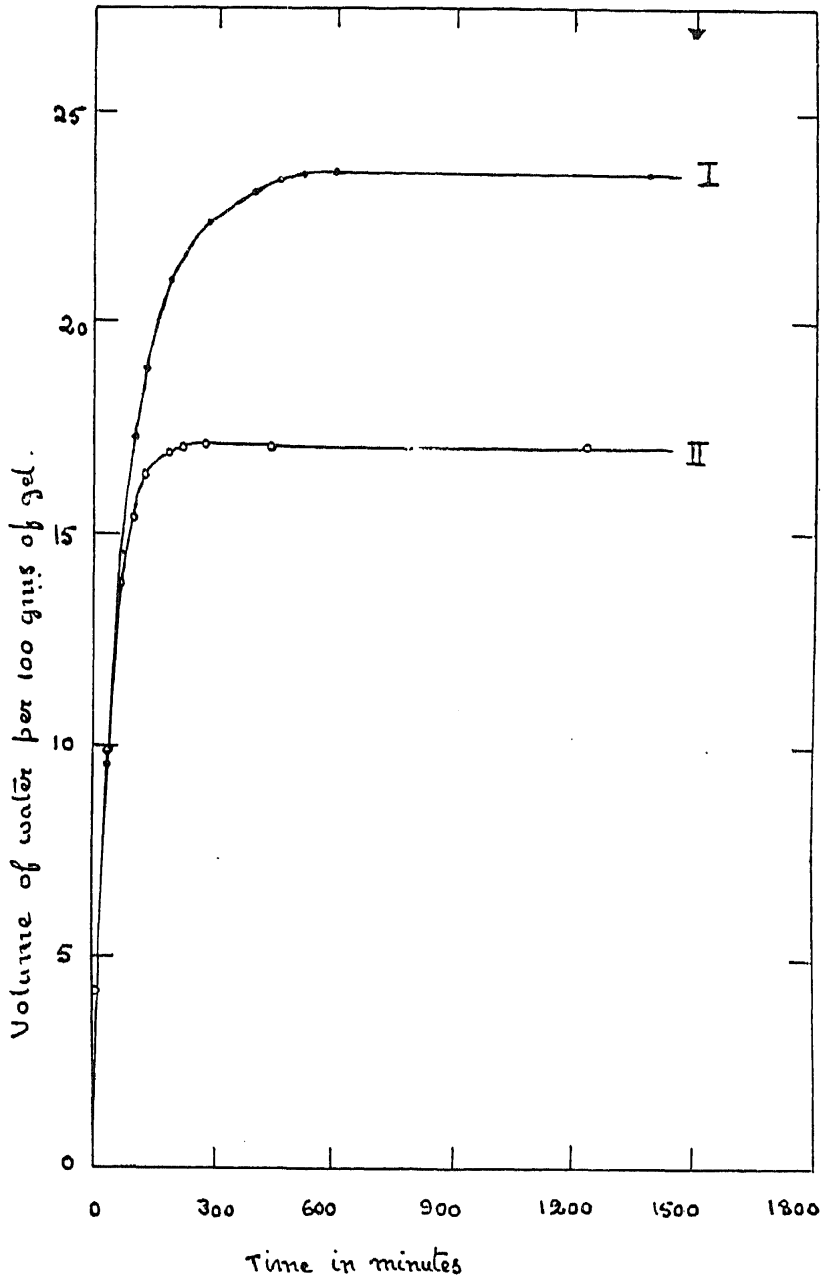

FIG. 2.

I. Glassy silica gel and water. II. Chalky silica gel and water.

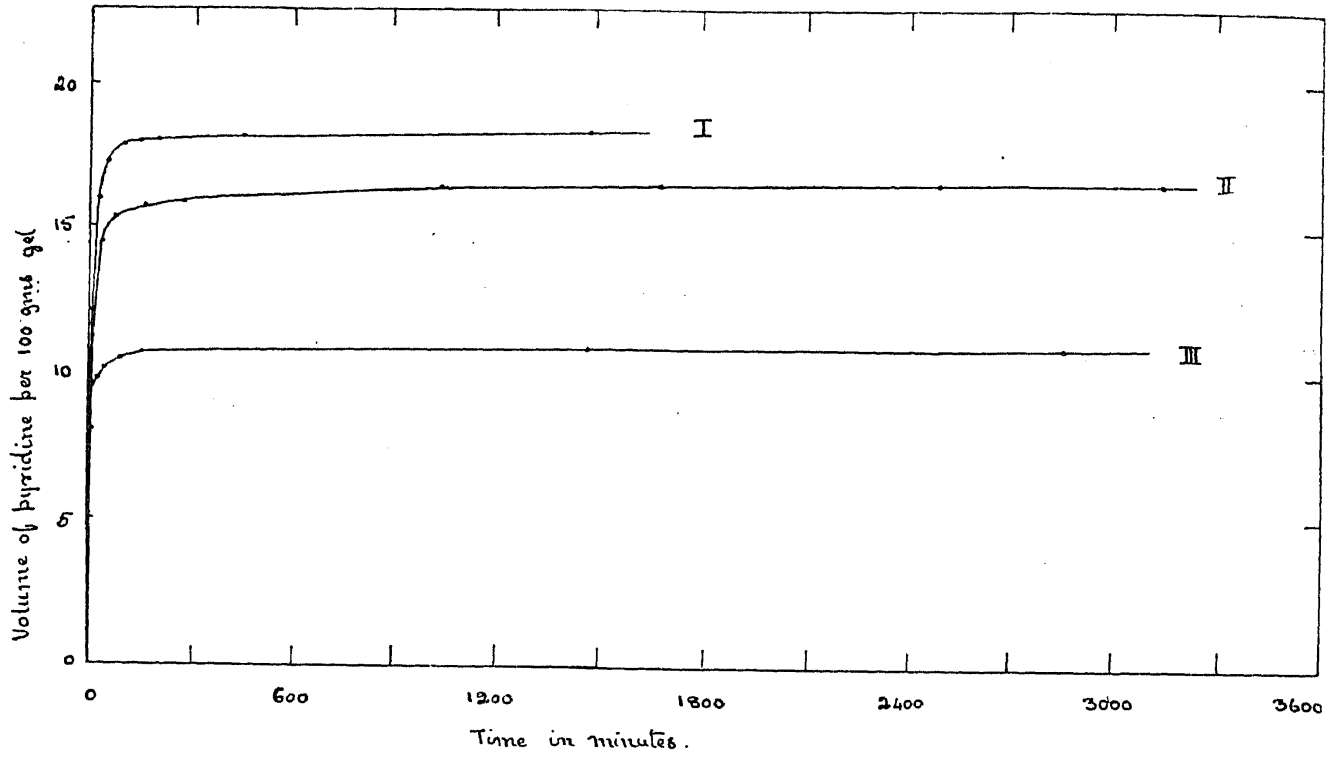

FIG. 3.

I. Alumina gel (activated at 500° C.) and pyridine.
II. Alumina gel (activated at 400° C.) and pyridine.
III. Alumina gel (activated at 850° C.) and pyridine.

TABLE I.

Adsorption of water on "glassy" silica gel activated at 450° C.

Time in minutes	Vol. in c.c. of H_2O at 40° C. held by 100 gm. of gel
30	9·50
60	14·51
90	17·28
120	18·91
180	20·98
270	22·33
390	23·04
450	23·38
510	23·57
590	23·42
1380	23·42

TABLE II.

Adsorption of water on "chalky" silica gel activated at 450° C.

Time in minutes	Vol. in c.c. of H_2O at 40° C. held by 100 gm. of gel
30	9·89
60	13·91
90	15·45
120	16·39
180	16·93
210	17·06
270	17·19
435	17·13
1230	17·13

TABLE III.

Adsorption of pyridine on alumina gel activated at 400° C.

Time in minutes	Vol. in c.c. of pyridine at 40° C. held by 100 gm. of gel
30	14·41
60	15·44
150	15·73
270	15·81
1050	16·51
1680	16·66
2490	16·66
3150	16·66

TABLE IV.

Adsorption of pyridine on alumina gel activated at 500° C.

Time in minutes	Vol. in c.c. of pyridine at 40° C. held by 100 gm. of gel
30	16·13
45	17·31
90	17·98
140	18·04
195	18·11
455	18·28
1485	18·42

TABLE V.

Adsorption of pyridine on alumina gel activated at 850° C.

Time in minutes	Vol. in c.c. of pyridine at 40° C. held by 100 gm. of gel
30	9·80
45	10·18
90	10·39
150	10·64
1485	10·79
2865	10·88

The activation of alumina gel at 850° C. could not be accomplished *in situ*. The gel was activated in an electric furnace in a current of dry air and then carefully transferred to the sorption tube.

Discussion.

Chalky gel has been known to have higher capillary volume than glassy variety, but to be poorer in fine capillaries. Liquid in fine capillaries has smaller vapour pressure than that held in broader ones. So in the glassy gel (which has fine capillaries) a larger amount of liquid (23·4 per cent.) is held at a corresponding pressure of 0·53 than in the chalky variety which retains only 17·1 per cent. At the saturation pressure, however, the chalky gel holds weight for weight nearly twice the volume of liquid retained by the glassy variety.

There has been considerable difference in the periods required for the attainment of equilibrium with the two gels. The glassy gel takes for water about 8 to 9 hours whereas chalky gel attains equilibrium within about $3\frac{1}{2}$ hours. This difference in the rates of adsorption is to be attributed to the size of the capillaries. The finer the capillaries greater is the time required for the attainment of equilibrium. According to Burrage[1] " the water condensed at the mouth of the smaller capillaries will retard free access into the interior and the capillaries require considerable time for complete filling."

The results on the adsorption of pyridine vapour by alumina gel activated at 400° C., 500° C. and 850° C. are noteworthy. The variation of the total capillary volume with the temperature of activation has already been indicated in Part I.[13] At saturation pressures the maximum adsorptive capacity is exhibited by gel activated at 850° C. At the corresponding pressure of 0·53 however this gel can take up only 10·9 per cent., though its total capillary volume is nearly 29·0 per cent. Gels activated at 400° C. and 500° C. have taken up (at corresponding pressure of 0·53) 16·7 per cent. and 18·4 per cent. though their total capillary volumes are 18·5 per cent. and 21·6 per cent. respectively. It is to be noted that though the total capillary volume rises with an increase in the temperature of activation, there is no similar increase in the volume of liquid adsorbed at a corresponding pressure of 0·53, the gel activated at 500° C. having higher adsorption than the other two gels. This shows that the capillaries in the gel activated at 850° C. are broader and do not get filled up to the same extent as the capillaries in the other two varieties. The effect of increasing the temperature of activation from 400° C. to 500° C. seems to be an increase in the total capillary space without any corresponding broadening of capillaries. Beyond 500° C. however, an increase in temperature of activation causes a considerable widening of pores. This is probably to be attributed to the loss of water from the monohydrate of alumina at temperatures above 500° C.

Summary.

A microspring balance of quartz fibre of the McBain-Bakr type has been used for studying adsorption of vapours of water and pyridine on gels of silica and alumina.

The difference in adsorption on "glassy" and "chalky" gels of silica has been accounted for, by the wider capillaries in the latter.

Adsorption of pyridine on alumina gels activated at 400° C., 500° C. and 850° C. has been studied. The differences noticed are attributed to the variation in capillary size.

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