SORPTIVE PROPERTIES OF FIBROUS SILICA GEL (SANTOCEL C) ACTIVATED AT DIFFERENT TEMPERATURES

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THE mode of preparation and treatment of sorbents have been reported by earlier workers to influence the nature and extent of sorption. Precipitated silica gel obtained by mixing sodium silicate and ammonium chloride solutions has been found to differ markedly in shape of the isotherms and the size and position of the hysteresis loops from glassy silica gel obtained from set silicic acid jelly of a mixture of sodium silicate and hydrochloric acid solutions.[1] Weiser and collaborators[2] have reported that if hydrous oxide gels are prepared by mixing boiling solutions of the reactants, the hysteresis effect, obtained in the sorption and desorption of water, is eliminated. Such elimination has been reported with silica gel in particular. Krishnappa and others[3] have studied that when silica gel is activated at different temperatures varying from 35° to 1,000°, its sorptive capacity for water first decreases upto 140°, remains practically constant from 140° to 500° and suffers a marked decrease at 1,000°.

The new form of silica gel—fibrous silica gel (Trade name Santocel C) produced by Monsanto Company, U.S.A.—has been used in the earlier investigations by the authors.[4] With this new form of silica gel, the effect of variation of the activation temperature on the sorptive properties has been studied and presented in this paper.

The study of sorption-desorption hysteresis of methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols at 35° on fibrous silica gel activated at 250° has been presented in the previous paper.[4] In the present paper a similar study has been made with the same sorbates at 35° on fibrous silica gel activated at 450° and the results are compared. The hysteresis loops of water and carbon tetrachloride with the two gels have also been included. The quartz fibre spring technique[5,6] has been employed in the present investigations.

RESULTS AND DISCUSSIONS

In all the cases the hysteresis loop is permanent and has been reproduced upto the 3rd cycle of sorption and desorption. In the case of ethyl alcohol, sorptions and desorptions were tried upto 5th cycle. The permanent and reproducible hysteresis loops obtained with the two samples activated at 250° and 450° are shown in Figs. 1 and 2 respectively to facilitate a comparative study. In these figures the isotherms are presented by plotting the volume of sorbate taken per 100 g. of gel against the relative vapour pressure.

At the end of the first cycle of sorption and desorption the gels retain some amount of water irreversibly in spite of several hours of evacuation. The amounts of bound water held by the two samples of silica gel activated at 250° and 450° are 2·5 cm.[3] and 1·4 cm.³/100 g. of gel respectively. The small volume of water irreversibly held may be chemisorbed. The sorptive capacities of the two samples at saturation pressure for the different sorbates are given in Table I.

TABLE I
Sorptive capacities of fibrous silica gel in cm.³/100 g.

		Activated at 250°	Activated at 450°
Water	..	64·0	62·2
Carbon tetrachloride	..	50·0	56·8
Methyl alcohol	..	33·0	52·0
Ethyl alcohol	..	33·3	61·2
n-Propyl alcohol	..	38·7	54·6
n-Butyl alcohol	..	19·0	21·4
n-Amyl alcohol	..	21·0	21·6

When the temperature of activation of the silica gel is raised from 250° to 450°, the sorption values at saturation pressure of methyl, ethyl and n-propyl alcohols have appreciably increased, that of carbon tetrachloride has increased slightly, whereas the values of other sorbates remain practically the same.

APPLICATION OF BET EQUATION AND MONOLAYER CAPACITIES

Excepting water and carbon tetrachloride, the sorption isotherms of the five aliphatic alcohols have clearly defined "knees". According to BET theory,[7] the "knee" signifies the transition from monomolecular to multimolecular sorption. The BET equation has been applied to the isotherms. BET plots were

straight lines. From the slope and intercept of the lines, the monolayer capacities x_m have been calculated. The value of monolayer capacity was also read out directly from the isotherms with reasonable accuracy[8,9] and is denoted by x_B. The values of monolayer capacities x_m and x_B for the five alcohols and the relative vapour pressures at which the monolayers are fully formed have been given in Table II.

TABLE II

Monolayer capacities x_m *and* x_B *in g. per g. of sorption and the corresponding relative vapour pressures*

	Silica gel activated at 250°			Silica gel activated at 450°		
	x_m	x_B	p/p_0	x_m	x_B	p/p_0
Methyl alcohol	0·016	0·016	0·05	0·017	0·016	0·05
Ethyl alcohol	0·018	0·017	0·05	0·022	0·023	0·06
n-Propyl alcohol	0·028	0·028	0·10	0·028	0·028	0·10
n-Butyl alcohol	0·035	0·032	0·13	0·034	0·036	0·10
n-Amyl alcohol	0·041	0·041	0·22	0·037	0·037	0·16

The agreement is good between the values of x_m and x_B for each alcohol with the two samples of gel activated at 250° and 450°.

MONOLAYER CAPACITY AND SPECIFIC SURFACE

From the monolayer capacity, the specific area of the sorbent is calculated as described in the earlier paper.[4] The molecular diameter $D_{spherical}$ is assumed for calculating the molecular cross-section. Knowing the molecular cross-sections of the five aliphatic alcohols and their monolayer capacities x_m, the specific

surface areas of the two gels are obtained. The results are shown in Table III.

TABLE III

Specific surface of fibrous silica gel considering alcohol molecules as spheres

	Molecular cross-section in $Å^2$	Specific surface in m^2/g of fibrous silica gel	
		Activated at 250°	Activated at 450°
Methyl alcohol	21·2	65·5	68·4
Ethyl alcohol	27·0	63·4	78·3
n-Propyl alcohol	31·4	86·7	86·7
n-Butyl alcoh l	36·0	103·4	99·6
n-Amyl alcohol	40·2	175·4	101·7

In both the gels, the value of the specific surface goes on increasing from methyl to n-amyl alcohol. This is due to the incorrectness of assuming the five aliphatic alcohol molecules as spheres. Actually the aliphatic alcohol molecules are linear in shape increasing in length from methyl alcohol to n-amyl alcohol. It is not strictly correct to assume the cubical or spherical shape for the molecules. The linear adsorbed molecule can be held on the surface either perpendicular or parallel to the surface. Assuming that the alcohol molecule is a rectangular rod, it is necessary to calculate the cross-section area of the rod and also the area of one of the four sides along the length of the rod.

The thickness[10] of the hydrocarbon chain is 4·55 Å. Therefore, the thickness of all the five alcohols is assumed to be the same. From the volume of the molecule D^3 and its thickness 4·55 Å, the length of the linear molecule can be calculated. The area of the end and the side along the length of the linear molecule are also calculated and are shown in Table IV.

TABLE IV

Specific surface of fibrous silica gel considering alcohol molecules as linear

	Diameter in Å	Length of the molecule in Å	Cross-section in $Å^2$	Area of side in $Å^2$	Specific surface in m^2/g of gel			
					Activated at 250°		Activated at 450°	
					Molecules perpendicular to surface	Molecules parallel to surface	Molecules perpendicular to surface	Molecules parallel to surface
Methyl alcohol	4·6	4·7	20·7	21·4	64·1	66·3	66·9	69·2
Ethyl alcohol	5·2	6·8	20·7	30·9	48·5	72·4	58·4	87·2
n-Propyl alcohol	5·6	8·5	20·7	38·5	57·2	106·8	57·2	106·8
n-Butyl alcohol	6·0	10·4	20·7	47·5	59·4	136·2	57·2	131·2
n-Amyl alcohol	6·3	12·1	20·7	55·0	57·3	152·0	52·4	139·0

The specific areas calculated by assuming both the modes of sorption have also been shown in the table.

The following interesting conclusions emerge from the results of Table IV. In both the gels, the values of specific surface obtained for the five alcohols are practically the same if oriented sorption perpendicular to the surface of the linear alcohol molecules is assumed. If oriented sorption parallel to surface is assumed, the value of the specific surface goes on increasing from methyl to *n*-amyl alcohol. Therefore it follows that sorption of the five aliphatic normal alcohols in the monolayers on the surface of fibrous silica gels activated at 250° and 450° are of the oriented type perpendicular to surface.

Secondly, for this oriented type of sorption perpendicular to surface, the specific surface values obtained of the gel activated at 250° are almost the same as those of gel activated at 450°. Variation in the temperature of activation has not made any difference in specific surface area of the gel.

SORPTION-DESORPTION HYSTERESIS

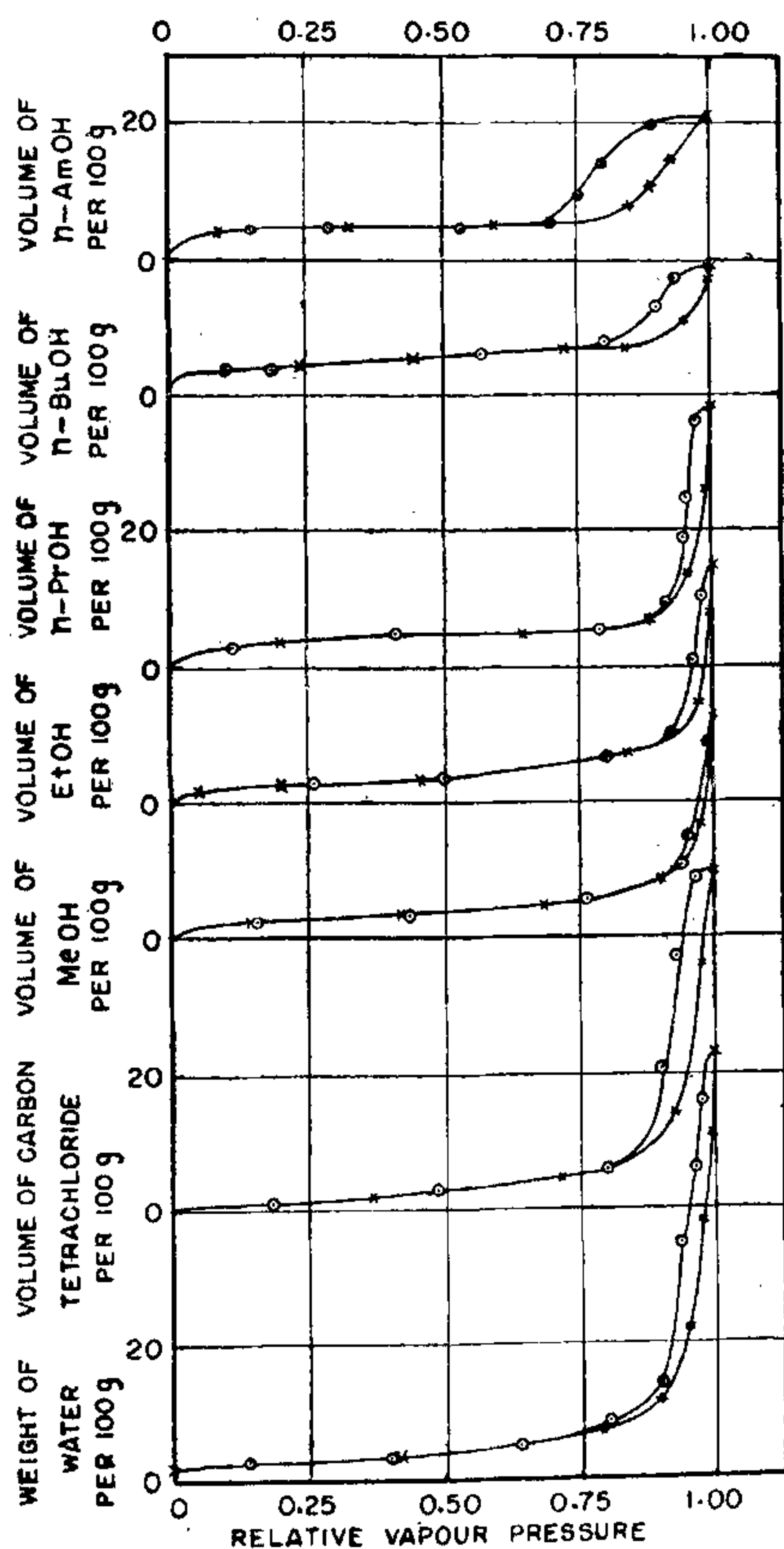Figures 1 and 2 reveal that the hysteresis loops of the two gels activated at 250° and

FIG. 1. Sorption and desorption on fibrous silica gel activated at 250° of water, carbon tetrachloride, methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl alcohols.
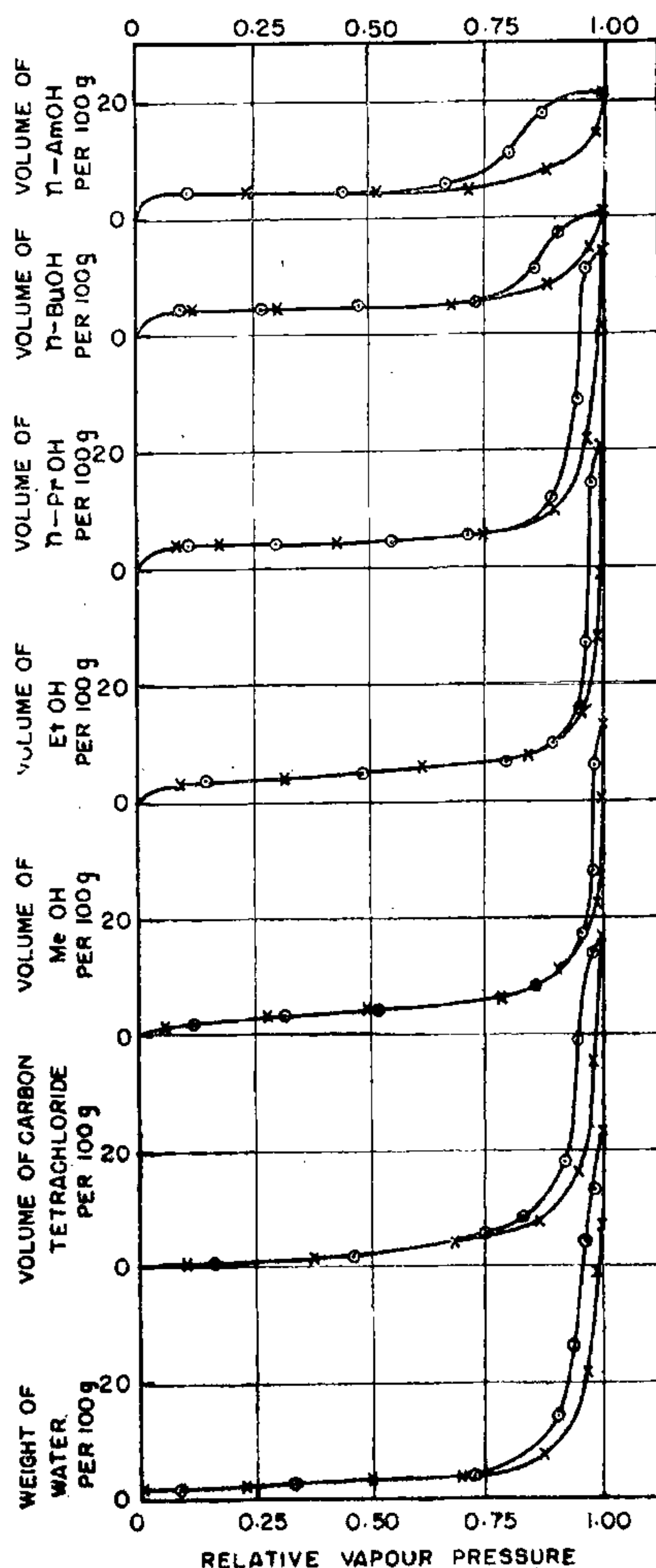

FIG. 2. Sorption and desorption on fibrous silica gel activated at 450° of water, carbon tetrachloride, methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl alcohols.

2

450° for any particular alcohol are almost identical in shape and point of commencement of the loop. There are two theories of sorption and desorption hysteresis—Cohan's theory[11] and the Cavity theory.[5,12] The applicability of Cohan's theory to the hysteresis loops of the five alcohols with silica gel activated at 250° and 450° has been studied. The values of molecular diameters $D_{Cohan's\ theory}$ have been calculated and are shown along with $D_{spherical}$ in Table V.

TABLE V

Molecular diameters D in Å of fibrous silica gel

	$D_{spherical}$	$D_{Cohan's\ theory}$	
		With gel activated at 250°	With gel activated at 450°
Water ..	3·5	15·5	14·6
Carbon tetrachloride	6·1	43·3	33·6
Methyl alcohol ..	4·6	52·2	52·2
Ethyl alcohol ..	5·2	47·2	47·2
n Propyl alcohol ..	5·6	41·2	41·2
n-Butyl alcohol ..	6·0	33·2	29·5
n-Amyl alcohol ..	6·3	28·8	35·7

In all the cases the values of D obtained by the application of Cohan's theory are higher than $D_{spherical}$ indicating the inapplicability of Cohan's theory to the results.

The cavity theory postulates that hysteresis effect is due to entrapping of liquid sorbate in the cavity during desorption until the relative vapour pressure corresponding to the neck of the cavity is reached. The shape and position of the hysteresis loop depends upon the shape and size of cavities.

PORE SIZE DISTRIBUTION

According to the cavity theory of hysteresis, the desorption curve of hysteresis loop indicates the neck radius and sorption curve the body radius of the cavity. The predominant neck and body radii of cavities are obtained from the midpoints of the steep parts of desorption and sorption curves respectively. The isotherms of water have been employed. Body and neck radii have been calculated by the application of Kelvin equation. The values of both the samples are shown in Table VI. The smallest neck radius corresponding to the point of inception of the hysteresis loop is also shown.

TABLE VI

Pore size distribution in Å of fibrous silica gel

	Smallest neck radius	Predominant neck radius	Predominant body radius
Gel activated at 250°	31·0	150·0	380·0
Gel activated at 450°	29·2	137·4	393·4

The results show that the values of smallest neck radius, the predominant cavity body and neck radii remain almost the same on heating fibrous silica gel from 250° to 450°. Higher temperature has not changed markedly the porous structure of fibrous silica gel. Similar results have been reported by Milligan and Rachford.[13] In their silica gel, hysteresis loop is not destroyed by moderate or even excessive heat treatment. However, heat of 400° to 600° actually increased the area of the loop.

1. Krishnappa, T., Subba Rao, K. and Sanjiva Rao, B., *Proc. Ind. Acad. Sci.*, 1947, **25**, 181.
2. Weiser, Milligan and Holes, *J. Phys. Chem.*, 1942, **46**, 586 & 1051.
3. Krishnappa, T., Subba Rao, K. and Sanjiva Rao, B., *Proc. Ind. Acad. Sci.*, 1947, **25**, 174.
4. Subba Rao, K. and Das, B., *Curr. Sci.*, 1968, **37**, 274.
5. —, *J. Phys. Chem.*, 1941, **45** 500.
6. — and Das, B., *Ibid.*, 1968, **72**, 1222.
7. Brunauer, S., Emmett, P. H. and Teller, E., *J. Am. Chem. Soc.*, 1938, **60**, 309.
8. Emmett, P. H. and Brunauer, S., *Ibid.*, 1937, **59**, 1553.
9. Gregg, S. J. and Sing, K. S. W., *Adsorption, Surface Area and Porosity*, Academic Press, London and New York, 1967, p. 54.
10. Moelwyn Hughes, E. A., *Kinetics of Reactions in Solutions*, Clarendon Press, Oxford, 1947, p. 7.
11. Cohan, L. H., *J. Am. Chem. Soc.*, 1938, **60**, 433.
12. McBain, J. W., *Ibid.*, 1935, **57**, 699.
13. Milligan, W. O. and Rachford, H H., Jr., *J. Phys. and Colloid Chem.*, 1947, **51**, 333.