

HYSTERESIS IN SORPTION

XI. Permanence of Sorption-Desorption Hysteresis

BY T. KRISHNAPPA,* K. SUBBA RAO† AND B. SANJIVA RAO,§ F.A.Sc.

(Department of Chemistry, Central College, Bangalore, S. India)

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INTRODUCTION

VAN BEMMELEN²⁵ was the first to notice the phenomenon of hysteresis in sorption. Later, other workers like Zigmondy,²⁹ Anderson,⁸ Coolidge,⁴ Winnings and Williams,²⁸ Shiels,²¹ M. Gavack and Patrick,⁸ Uquhart,²⁴ Sheppard and Newsome,²⁰ McBain and Ferguson⁷ studied this effect. But for a long time the reality of the effect remained uncertain. By careful experiments on charcoal, Allmand and collaborators^{1,2} showed that the hysteresis effect was real. Working with hydrous oxides Lambert and co-workers also proved the reality of the phenomenon. Recently, Rao, K. S.⁹ has established, by extensive investigations on various porous adsorbents that the hysteresis effect is remarkably permanent and can be reproduced any number of times. Besides establishing the permanence and reproducibility of the effect, interesting phenomena such as drift,^{10, 11} and disappearance^{12, 13, 14, 22} of the hysteresis loop have been discovered. A new method of study of hysteresis called "scanning" of the loop has been developed.

Weiser and collaborators^{26, 27} have recently reported that if hydrous oxide gels are prepared by mixing boiling solutions of the two reactants, the hysteresis effect with reference to water vapour is completely eliminated. Such elimination has been reported with silica gel in particular.

Several explanations have been offered from time to time for the hysteresis effect. After making a critical study of these in a recent review,¹⁸ Rao concludes that the cavity concept affords the only general explanation of the hysteresis and all other related phenomena.^{6, 23}

In accordance with the cavity concept, a rigid porous adsorbent like silica gel should always show a permanent hysteresis effect. Complete elimination of the hysteresis effect without a marked fall in the sorptive capacity is improbable. Weiser's observations however are in contradiction

* Mysore Government Scholar, University of Sheffield, Sheffield.

† Senior Research Fellow of the National Institute of Sciences of India.

§ Principal and Professor of Chemistry, Central College, Bangalore.

to this view. Therefore a careful study of sorption and desorption has been made in this laboratory on gels of silica, alumina and titania, prepared by mixing the boiling hot solutions of the reactants in accordance with the procedure adopted by Weiser and collaborators (*loc. cit.*).

EXPERIMENTAL

Composition of sodium silicate

On analysis, the sodium oxide and silicon dioxide ratio was found to be 1.02 in the meta silicate and 0.52 in the water glass used.

Silica gels

Silica gel A (precipitated at 25° C.).—80 c.c. of sodium silicate solution (containing 0.13 gm. of silicon dioxide per c.c.) were added slowly to 100 c.c. of acetic acid solution containing 30 c.c. of glacial acetic acid, the mixture being stirred vigorously by an electrical stirrer. The mixture was kept overnight, then mixed with water, filtered and washed free from acid. The washed gel was dried in air for some hours at room temperature (25° C.). Gels were prepared both from sodium metasilicate and water glass.

Silica gel B (precipitated at 100° C.).—The sodium silicate solution was first boiled for six hours under reflux. Boiling hot solutions of the silicate and acetic acid were then mixed, the concentrations and quantities of solutions being the same as in the above experiment. Gels were prepared from both metasilicate and water glass by the above procedure.

Silica gel C (Gel B treated with boiling water).—A portion of the washed silica gel B was refluxed in boiling water for 96 hours. After this treatment the gel was washed and dried in air.

Silica gel D (gel B heated in water at 120° C.).—Another portion of washed silica gel B was suspended in water and heated to 120° C. in an autoclave for 3 hours. The gel was washed and dried in air.

Titania gels

Gel A.—50 gm. of titanium tetrachloride were dropped into concentrated hydrochloric acid. The mixture was diluted so that the resulting solution was 0.5 N with respect to titanium tetrachloride and 0.2 N with respect to hydrochloric acid. 0.7 N ammonium hydroxide was added at room temperature (25° C.) in a thin stream to the titanium tetrachloride solution, the liquid being vigorously stirred. Two per cent. excess of ammonium hydroxide was added. The precipitate was filtered off, washed and dried in air.

Gel B.—The titania gel was prepared in the same way as indicated above but the precipitation was conducted in boiling hot solutions.

Alumina gels

Gel A.—To 0.5 N solution of aluminium sulphate, excess of 0.5 N ammonium hydroxide was added at room temperature (25° C.) in a thin stream while stirring the former. The mixture was filtered, washed free from sulphate and dried in air.

Gel B.—The alumina gel was prepared in the same way but by precipitation in boiling hot solutions.

Sorption and desorption of water vapour

The quartz fibre spring technique⁹ was employed in the investigations. Distilled water kept in the bulb of the sorption apparatus was rendered air free by evaporating a portion of the water in vacuum obtained by the Cerco Hyvac pump.

The air-dried gel was placed in the bucket and the spring was introduced into the sorption tube. The system was then evacuated at 30° C. for 5 or 6 hours at a pressure of 10^{-3} mm.

After degassing the gel, sufficient amount of water vapour from the bulb was introduced into the sorption tube and the stopcock was closed. The gel was allowed to attain equilibrium with water vapour. The equilibrium pressure of the system and the stretch of the spring were measured. More water was introduced and measurements were continued until the saturation pressure was reached. Desorption was then carried out by removing sufficient amount of water vapour with the aid of the hyvac pump. After the attainment of equilibrium, the pressure and stretch were measured. The desorption was continued until zero pressure was reached. For the attainment of equilibrium, the appropriate time required was about 6 hours for silica gel, 4 hours for titania and 3 days for alumina. In actual practice however, 10 hours were allowed for silica gel, 6 hours for titania and 4 days for alumina. A series of sorptions and desorptions of water vapour at 30° C. on the various gels gave permanent hysteresis loops (Figs. 1 to 10).

Residual water

In each system, at the end of the experiment when the gel was at the zero point after desorption, it was removed for the estimation of the residual water. The water content of the gel was determined by igniting to constant weight in a platinum crucible. The residual water in each gel is indicated in the corresponding graph.

DISCUSSION

Hysteresis in sorption has been explained on the basis of the cavity concept. In any rigid porous system, there are open pores as also the capillaries with constricted ends. The latter types of capillaries—the cavities, are responsible for the hysteresis effect. Existence of only one type, *i.e.*, either the cavity or the open pore in a porous system is highly improbable in a random distribution. Silica gel prepared by us in close conformity with the procedure adopted by Weiser, Milligan Holes and Simpson has in

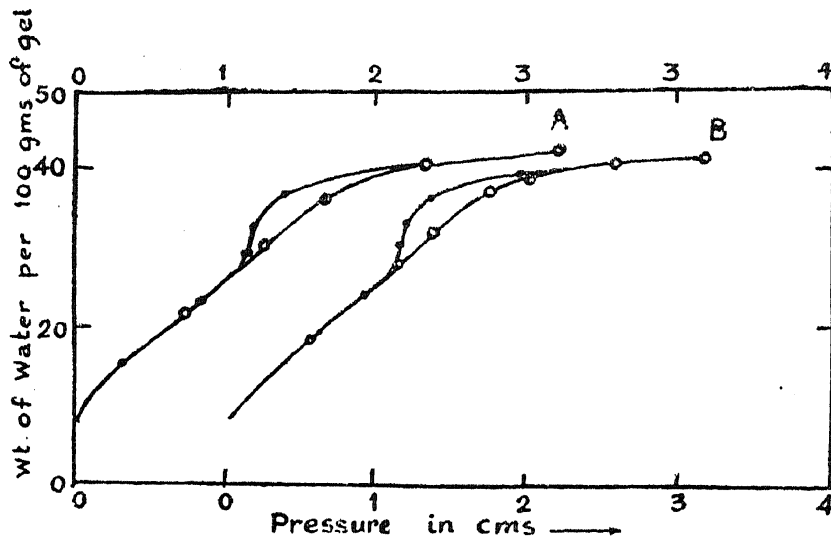


FIG. 1. Sorption and desorption of water vapour on silica gel from metasilicate precipitated at 25° C. (A. 2nd cycle, B. 3rd cycle).

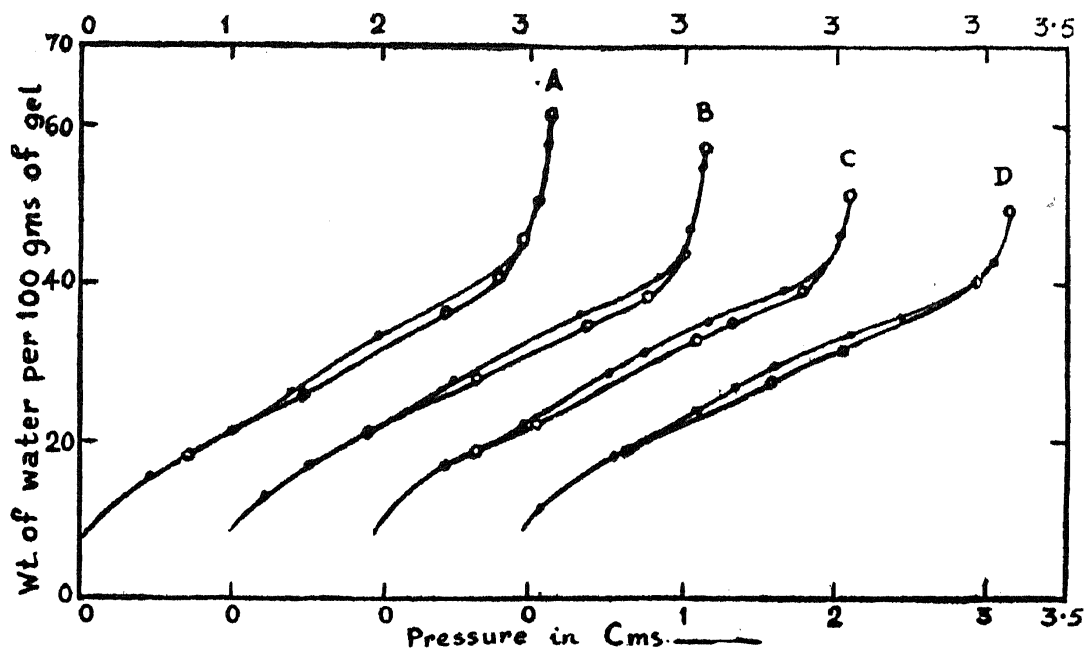


FIG. 2. Sorption and desorption of water vapour on silica gel from metasilicate precipitated at 100° C. (A. 1st cycle, B. 2nd cycle, C. 3rd cycle, D. 4th cycle).

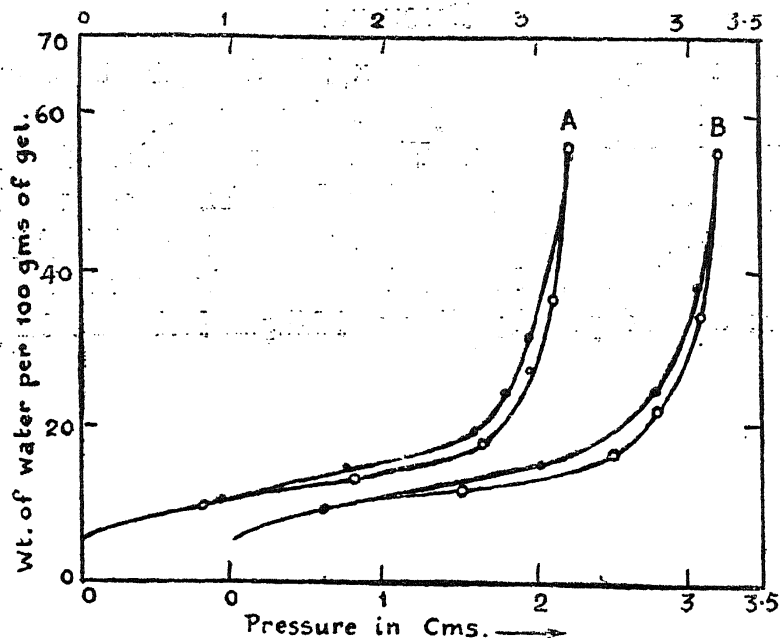


FIG. 3. Sorption and desorption of water vapour on silica gel from metasilicate precipitated at 100°C . and heated in boiling water (A. 1st cycle, B. 3rd cycle).

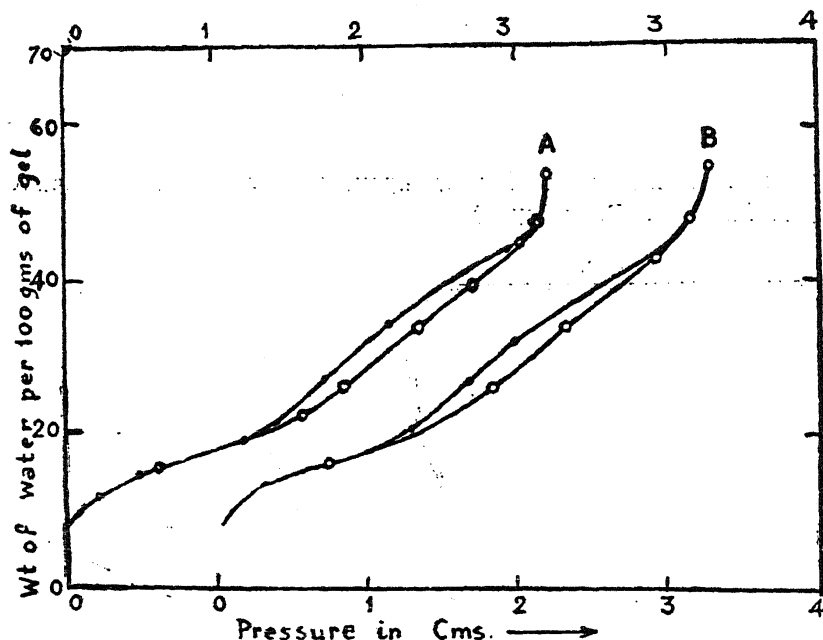


FIG. 4. Sorption and desorption of water vapour on silica gel from metasilicate precipitated at 100°C . and gel heated in water at 120°C . (A. 1st cycle, B. 2nd cycle).

all cases been found to show a permanent hysteresis effect. Gel precipitated from metasilicate at 100°C ., with previous boiling for 6 hours has given permanent hysteresis loop (Fig. 2), though smaller in size than that exhibited by the gel precipitated at 25°C . (Fig. 1). A sample of air-dried gel, precipitated at 100°C ., was boiled in water under reflux for 96 hours. The gel

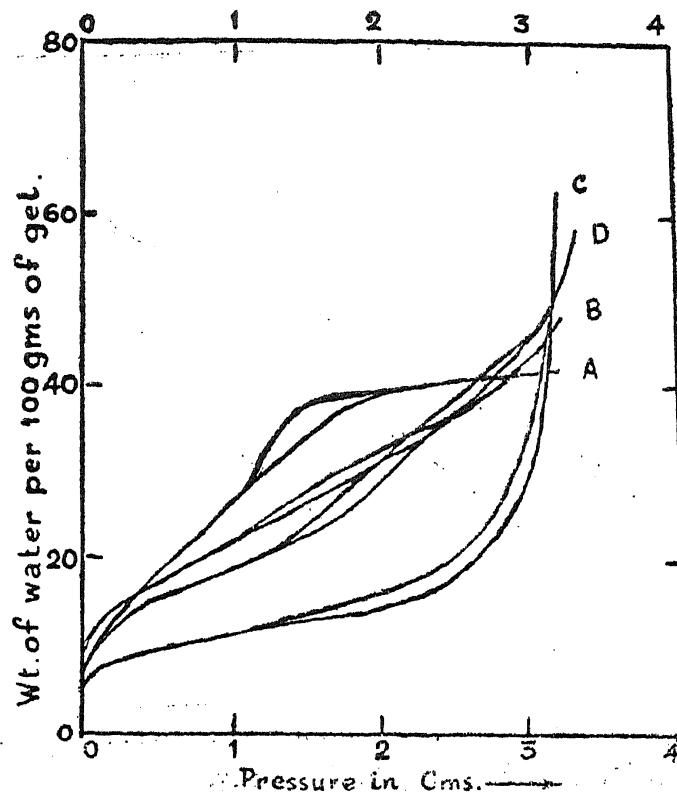


FIG. 5. Sorption and desorption of water vapour on silica gel from metasilicate and heated in boiling water and heated in water at 120° C.

- A. Gel precipitated at 25° C.
- B. " " " 100° C.
- C. " " " "
- D. " " " "

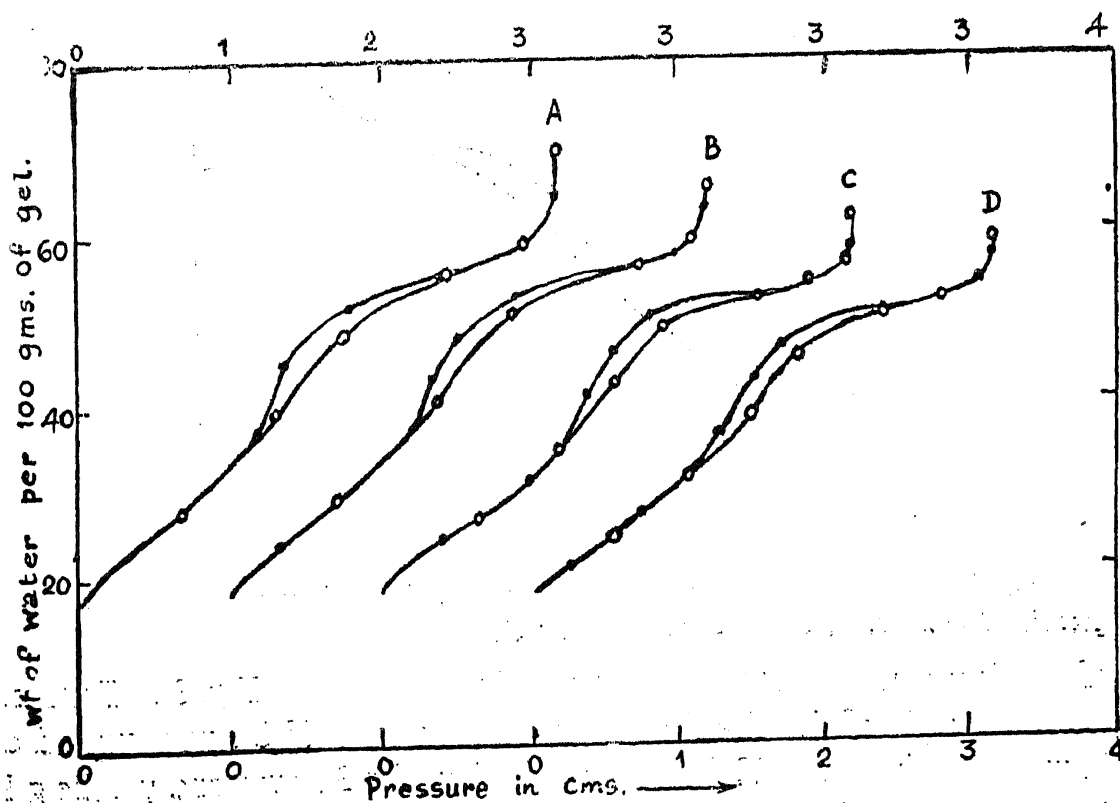


FIG. 6. Sorption and desorption of water vapour on silica gel from water glass precipitated at 25° C. (A. 1st cycle, B. 2nd cycle, C. 3rd cycle, D. 4th cycle).

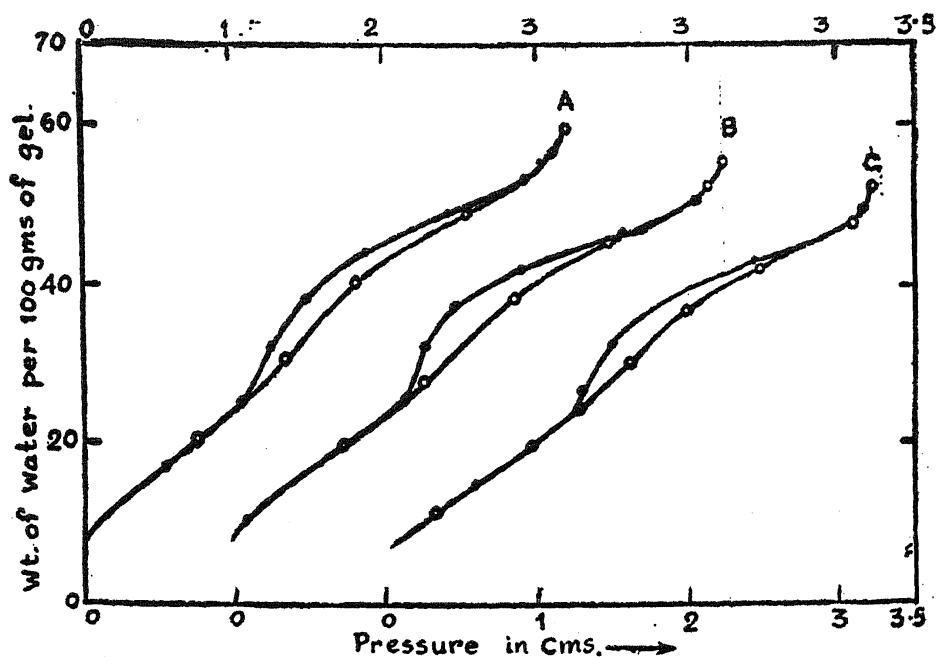


FIG. 7. Sorption and desorption of water vapour on silica gel from water glass precipitated at 100° C. (A. 1st cycle, B. 3rd cycle, C. 11th cycle).

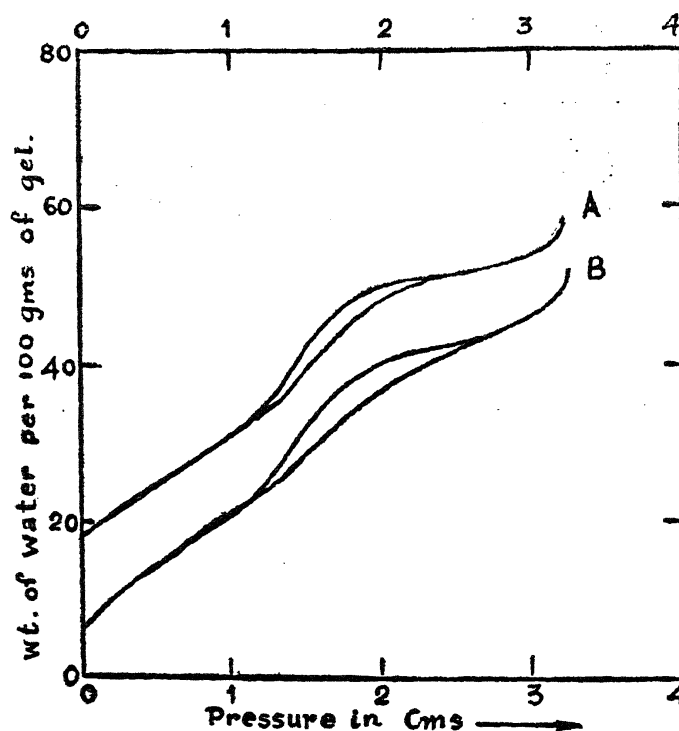


FIG. 8. Sorption and desorption of water vapour on silica gel from water glass (A. Gel precipitated at 25° C. B. Gel precipitated at 100° C).

after this treatment showed a permanent hysteresis loop (Fig. 3). Further, another sample of the air-dried gel precipitated at 100° C., was suspended in water and heated to 120° C., in an autoclave for 3 hours and yet the gel gave a permanent hysteresis loop (Fig. 4).

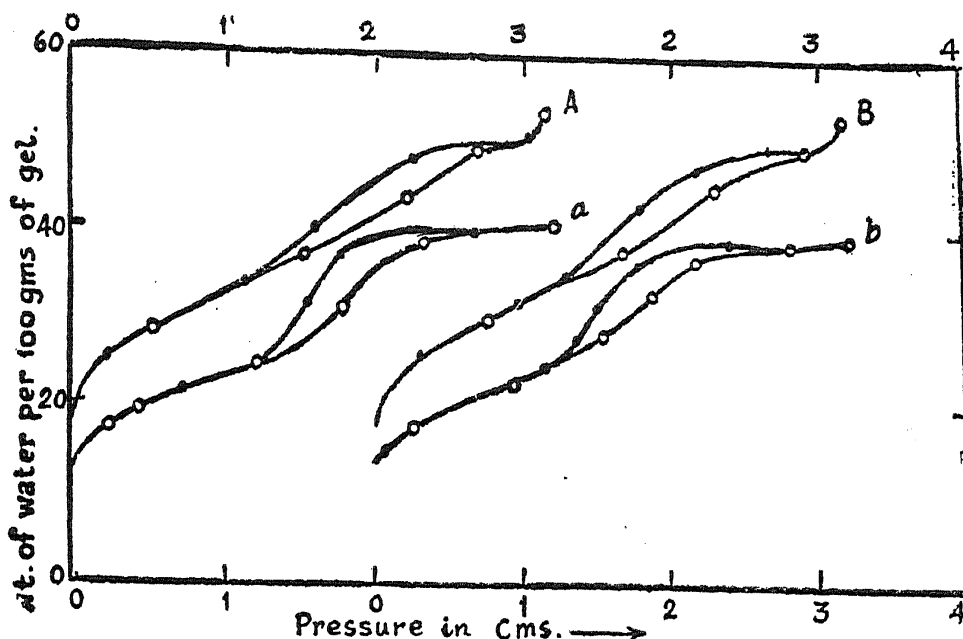


FIG. 9. Sorption and desorption of water vapour on Titania gel
Gel precipitated at 25° C (A. 1st cycle. B. 2nd cycle)
" " at 10° C. (a. 1st cycle, b. 2nd cycle).

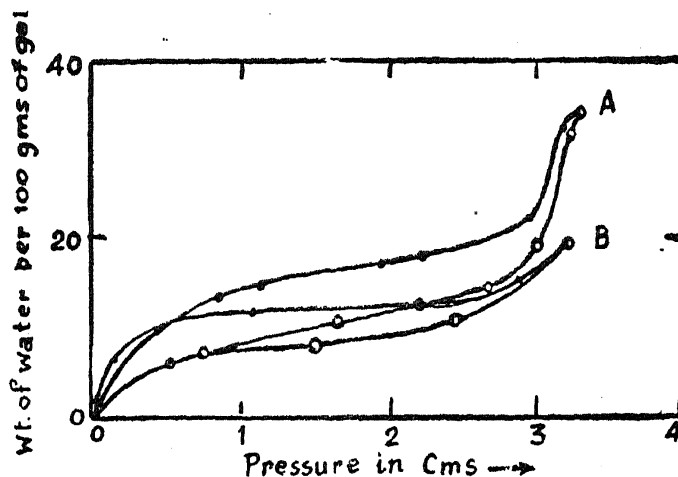


FIG. 10. Sorption and desorption of water vapour on alumina gel
A. Gel precipitated at 25° C. (1st cycle).
B. " " 100° C. (1st cycle).

Similarly, gels precipitated from water glass at 25° C., and 100° C. (with previous boiling of the water glass solution under reflux) have shown permanent hysteresis loops (Figs. 6 and 7). These loops have been studied up to the eleventh cycle of sorption and desorption.

Sorption studies with gels of titania and alumina precipitated at 25° C. and 100° C. have also shown permanent hysteresis loops (Figs. 9 and 10). In none of the systems studied above, is complete elimination of the hysteresis loop noticeable. Though in their paper, Weiser and collaborators conclude, that aging the sol, at the boiling point before coagulation to gel, even eliminates the sorption-desorption hysteresis with water, a careful scrutiny of the hysteresis loops obtained by them (with gels of hydrous oxides of silica

from water glass,²⁶ silica from metasilicate,²⁶ tantalum pentoxide,²⁷ stannic oxide²⁷ and titanium dioxide²⁷ reveals that in none of these systems is there a complete elimination of the hysteresis loop.

The only system in which a complete elimination of the hysteresis effect is reported by Weiser and collaborators is with silica gel prepared from metasilicate at 100° C. with previous boiling of the silicate solution for 3 hours. But in this case, only one cycle of sorption and desorption seems to have been studied and even in this instance, there is a small loop and this apparently has not been noticed by the authors.

There is therefore no adequate experimental evidence supporting the view that there can be a complete elimination of the hysteresis effect. In the light of the cavity concept, a complete elimination of the hysteresis effect is in fact, improbable in a rigid porous adsorbent. It may be pointed out that though Weiser and co-workers have obtained gels with very small hysteresis loops, the gels show no marked diminution in sorptive capacity. Decrease in the hysteresis effect must in our opinion, be accompanied by a corresponding reduction in sorptive capacity. It is only in systems of elastic gels with solvating liquids like rice-water,^{12, 13} dhal-water,¹² gum arabic-water,¹⁴ gelatin-water,²² casein-water,²² and egg albumin-water²² that complete elimination or disappearance of the hysteresis loop, without a diminution in the sorptive capacity is possible. In a rigid porous gel however, hysteresis in sorption is a rule rather than an exception. If in a rigid gel there is a rule rather than an exception. If in a rigid gel there is complete elimination of the hysteresis effect, the total sorptive capacity being unaffected, it is a case of the absence of superheating¹⁹ of liquid in cavities and no such instance is known of the elimination of superheating by altering the mode of preparation of the gel.

In the several systems studied, it is noticed that with an increase in the temperature of precipitation of the silicic acid, there are changes in the total sorptive capacity, the size, shape and position of the hysteresis loops. But there is no strict correlation between these changes and the temperature of precipitation.

The gels of the hydrous oxides of silica from water glass (Fig. 8), silica from sodium metasilicate (Fig. 5), titania (Fig. 9) and alumina (Fig. 10) precipitated at 100° C., sorb less water (particularly at pressures below saturation) than the corresponding gels precipitated at 25° C. Sorption and desorption curves obtained by Weiser and co-workers for gels of silica from water glass,²⁶ silica from sodium metasilicate,²⁶ stannic oxide²⁷ and titania²⁷ indicate a similar decrease in sorptive capacity by raising the temperature

of precipitation from 0° C. to 100° C. Tantalum pentoxide²⁷ however, is an exception and shows an increase in the amount of water sorbed by raising the temperature of precipitation from 0° C. to 100° C. Barring this exceptional behaviour of tantalum pentoxide, the temperature of precipitation has a noticeable effect on the capillary space in the precipitated gels. A rise in the temperature of precipitation affects the nature and the extent of the capillary space. Thus the sorptive capacity of the gels generally decreases with an increase in the temperature of precipitation. In a few cases however, though the sorptive capacity at lower relative vapour pressures has decreased, the sorptive capacity of gel at saturation pressure has actually increased. This indicates that wider capillaries have been formed in the gel at higher temperatures of precipitation.

In addition to lowering the sorptive capacity of gels, the temperature of precipitation has a marked influence in several cases, on the size, shape and position of the hysteresis loop. The loop of silica gel precipitated from metasilicate at 100° C. with previous boiling differs markedly in shape from that of gel precipitated at 25° C. (Fig. 5). The hysteresis loop of the gel heated in water to 120° C. differs in the same way from that of the gel at 25° C. With gel boiled in water for 96 hours, there is a similar change in the shape of the hysteresis loop and the change is very prominent. The positions of the hysteresis loops of the gels indicate, that the cavities in gel precipitated at 25° C. are concentrated in a fairly narrow range of capillary radius, whereas those of other gels are distributed over a wide range (Fig. 5). The hysteresis loop of silica gel precipitated from water glass at 100° C., though slightly bigger, is practically of the same shape as that of gel precipitated at 25° C. (Fig. 8). With titania and alumina the loops of gels precipitated at 100° C. are nearly the same in shape and size as those of gels precipitated at 25° C. (Figs. 9, 10).

With reference to the hysteresis loops obtained by Weiser and collaborators, it may be pointed out that the hysteresis loops of silica gels precipitated at 0° C., 25° C. and 63° C. from water glass are practically of the same size but that of the gel precipitated at 100° C. is negligibly small.²⁶ Gel precipitated at 25° C. from metasilicate shows a slightly bigger hysteresis loop than gel precipitated at 0° C. and the loop becomes smaller for gel formed at 100° C.²⁶ Tantalum pentoxide shows a slight decrease in the area of the hysteresis loop as the temperature of precipitation of the gel rises from 0° C. to 100° C.²⁷ Titanium dioxide gel also shows a similar change.²⁷ Stannic oxide gel however, forms an exception.²⁷ The loop of stannic oxide gel precipitated at 100° C. is nearly the same as, or slightly bigger than that

of gel precipitated at 0° C. The positions of the loops are markedly different and indicate that the cavities in the gel precipitated at 100° C. are wider than those in the gel precipitated at 0° C.

It may be pointed out, that there is no strict correlation between the temperature of precipitation of the gel and the size, shape and position of the hysteresis loop. In most of the systems studied, there is however, a general tendency for the area of the hysteresis loop to diminish with an increase in the temperature of precipitation of the gel, indicating a corresponding diminution in the total cavity volume.

In conclusion, it may be stated that there is no evidence of any complete elimination of the hysteresis loop. Higher temperature of precipitation renders a hydrous oxide gel less porous and there is a corresponding diminution in the number of cavities which are responsible for the hysteresis phenomenon.

SUMMARY

The effect of variation of the temperature of precipitation of gels of hydrous oxides of silica, titania and alumina on the hysteresis effect in the sorption of water vapour has been studied at 30° C. Gels have been obtained by precipitating the hydrous oxides at 25° C. and 100° C. with previous boiling of the silicate solution.

In all the systems studied, permanent hysteresis loops have been obtained. With increase in the temperature of precipitation, there has been a diminution in the sorptive capacity of gels for water at different partial pressures and in most of the systems the hysteresis loop suffers a diminution in size with a change in the shape and position of the loop. But in none of these systems, is any complete elimination of the loop noticeable. Gels precipitated at 100° C. are less porous than the gels precipitated at 25° C. and appear to have fewer cavities that are responsible for the phenomenon of hysteresis.

REFERENCES

1. Allmand, Hand and Manning .. *J. Phys. Chem.*, 1929, 33, 1694.
2. ——— and Chaplin .. *Proc. Roy. Soc. (Lond.)*, 1930, A 129, 264.
3. Anderson, J. S. .. *Z. Physik. Chem.*, 1914, 88, 264.
4. Coolidge .. *J. Amer. Chem. Soc.*, 1927, 49, 708.
5. Lambert and Foster .. *Proc. Roy. Soc. (Lond.)*, 1932, A 136, 363.
6. McBain .. *J. Amer. Chem. Soc.*, 1935, 57, 699.
7. ——— and Ferguson .. *J. Phys. Chem.*, 1927, 31, 564.
8. McGavack and Patrick .. *J. Amer. Chem. Soc.*, 1920, 42, 946
9. Rao, K. S. .. *J. Phys. Chem.*, 1941, 45, 500.
10. ——— .. *Ibid.*, 1941, 45, 522.

11. Rao, K. S. .. *Curr. Sci.*, 1939, 8, 546.
12. _____ .. *J. Phys. Chem.*, 1941, 45, 531.
13. _____ .. *Curr. Sci.*, 1939, 8, 256.
14. _____ .. *Ibid.*, 1940, 9, 19.
15. _____ .. *Ibid.*, 1939, 8, 468.
16. _____ .. *Proc. Ind. Acad. Sci.*, 1942, 6, 298.
17. _____ .. *Ibid.*, 1942, 6, 302.
18. _____ .. *J. Mys. Uni.*, 1943, 4, 1.
19. _____ .. *Curr. Sci.*, 1940, 9, 68.
20. Sheppard and Newsome .. *J. Phys. Chem.*, 1929, 33, 1817.
21. Shields .. *Ibid.*, 1929, 33, 1167.
22. Subba Rao, G. N., Rao, K. S., .. Hysteresis in Sorption XV, *Proc. Ind. Acad.*
and Rao, B. S. .. *Sci.*, 1947, 25, 190.
23. Taylor, H. S. .. *A Treatise on Physical Chemistry*, Macmillan
& Co., London, 1931, 2, 1661.
24. Urquhart .. *J. Textile Inst.*, 1929, 20 T, 125.
25. Van Bemmelen .. *Die Absorption*. Theodor, Stainkopf, Dresden,
1910.
26. Weiser, Milligan and Holes .. *J. Phys. Chem.*, 1942, 46, 586.
27. _____ and Simpson .. *Ibid.*, 1942, 46, 1051.
28. Winnings and Williams .. *Ibid.*, 1931, 35, 2915.
29. Zsigmondy .. *Z. Anorg. Chem.*, 1911, 71, 356.