90. *Comparative Isothermals of Water and Deuterium Oxide on Porous Solids.*

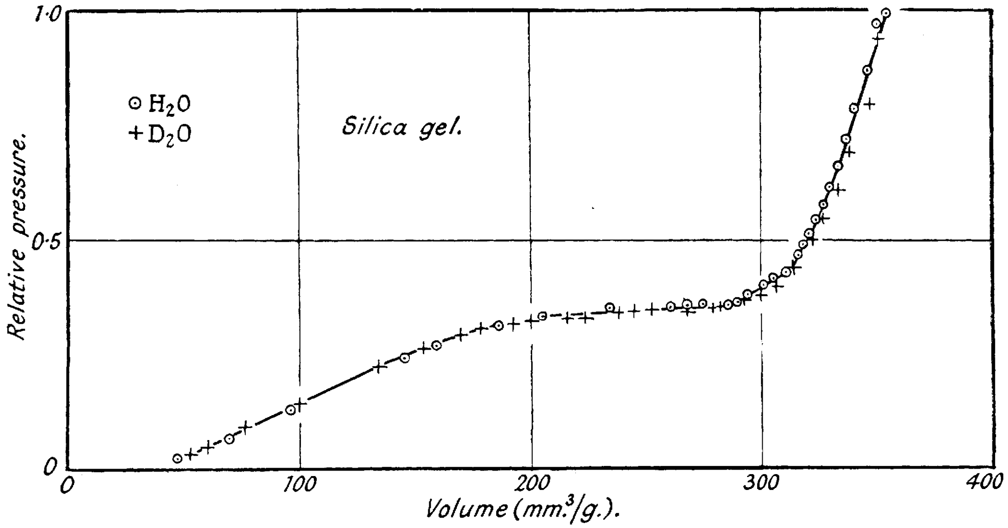
By D. N. Broad and A. G. Foster.

The adsorption isothermals of water and deuterium oxide have been compared at 25° on silica and ferric oxide gels and on charcoal. On each adsorbent the relative pressure–volume curves for the two liquids are identical. The results on the whole tend to support the capillary theory, although the behaviour of water on charcoal presents certain anomalies.

THE sorption of water by silica and ferric oxide gels has been investigated by Lambert and Foster (*Proc. Roy. Soc.*, 1931, *A*, **134**, 246; 1932, **136**, 363) and Foster (*Trans. Faraday Soc.*, 1932, **28**, 645) suggested that in these systems the shape of the isothermal is determined by the ratio of the diameter of the pores of the adsorbent to that of the adsorbed molecule. When this ratio is large, the " sorption " is mainly a capillary condensation process, the equilibrium pressures being determined by the Kelvin equation, $\boldsymbol{R}T \log_e p_s/p = 2M\gamma/\rho r$, where p_s is the saturation pressure of the pure liquid, M its molecular weight, γ its surface tension, and ρ its density, all at T° K., and r is the radius of the space in which capillary condensation occurs, which is less than the true pore radius by an amount equal to the thickness of the adsorbed layer.

The S-shaped isothermals of vapours adsorbed on ferric oxide gel are consistent with the view that, after the formation of an adsorbed layer one or two molecules thick, the remainder of the pore space fills up by capillary condensation (Foster, *Proc. Roy. Soc.*, 1934, *A*, **147**, 128). On most charcoals, however, water is the only substance which gives these S-shaped isothermals, other liquids giving " normal " isothermals to which the Langmuir equation is generally applicable. McBain (*J. Amer. Chem. Soc.*, 1930, **52**, 2198) pointed out that the formation of the unimolecular layer often leaves no room for further sorption of any kind, and suggested the term " persorption " to describe this special case. In discussing the isothermals of water on charcoal, McBain (" The Sorption of Gases by Solids," p. 148) rejects the capillary theory and attributes the anomalous behaviour of water to the polar nature of the molecule. This " polarisation " theory has, however, never been formulated quantitatively, and whereas King, James, Lawson, and Briscoe (J., 1935, 1545) predicted that the flat portion of the isothermals of heavy water on charcoal should lie at a lower relative pressure than that of the water isothermals, subsequent investigation by King and Lawson (*Trans. Faraday Soc.*, 1936, **32**, 478) failed to confirm this. The latter authors remark that " in view of the uncertainty of obtaining reproducible charcoal surfaces, no special significance can be given to the small differences between the isotherms." Actually, the similarity of the water and deuterium oxide curves is a significant argument in favour of the capillary theory. If we compare two liquids A and B at the same temperature, we should expect from the Kelvin equation that, when equal volumes are adsorbed and the pores filled to the same level (*i.e.*, $r_A = r_B$), then $\log_e \pi_A/\log_e \pi_B = V_A\gamma_A/V_B\gamma_B$, where π is the relative pressure and V the molar volume. Now these physical constants are known for both ordinary and heavy water, so the difference in the values of $V\gamma$ for the two liquids is easily calculated. For water at 25°, $V = 18{\cdot}06$, and for heavy water at 25° ($d = 1{\cdot}104$; Lewis and Macdonald, *J. Amer. Chem. Soc.*, 1933, **55**, 3057), $V = 18{\cdot}11$, so the molar volumes of the two liquids differ by only 0·03%. It is now fairly certain that the surface tension of heavy water does not differ appreciably from that of ordinary water, for although the original work of Selwood and Frost (*ibid.*, p. 4355) indicated a value some 7% lower, yet Lachs and Minkow (*Nature*, 1935, **136**, 186) reported values of 72·2 and 72·7 for heavy and ordinary water, respectively, at 25°, Timmermans and Bodson (*Compt. rend.*, 1937, **204**, 1804)

FIG. 1.



found identical values (72·9) at 20°, and Jones and Ray (*J. Chem. Physics*, 1937, **5**, 505) give the ratio for D_2O to H_2O as 0·99946 at 25°. It may therefore be assumed that the product $V\gamma$ for the two liquids is practically identical, so the relative pressures at corresponding volumes should be identical, and the isothermals plotted as relative pressure against volume adsorbed should coincide. The " reduced isothermals " of the two liquids on silica, ferric oxide, and " Dorsite " charcoal are in fact identical as shown by Figs. 1, 2, and 3.

The measurements on ferric oxide gel were continued down to about 0·02 mm. by using the Pirani gauge technique (see this vol., p. 360). Fig. 4 shows the low-pressure isothermals of the two liquids plotted as actual pressure against mols. adsorbed. The curves are again identical.

FIG. 2.

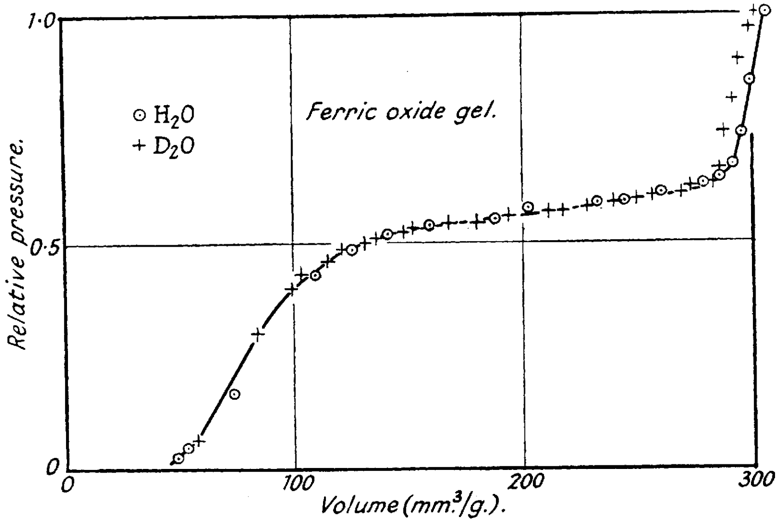
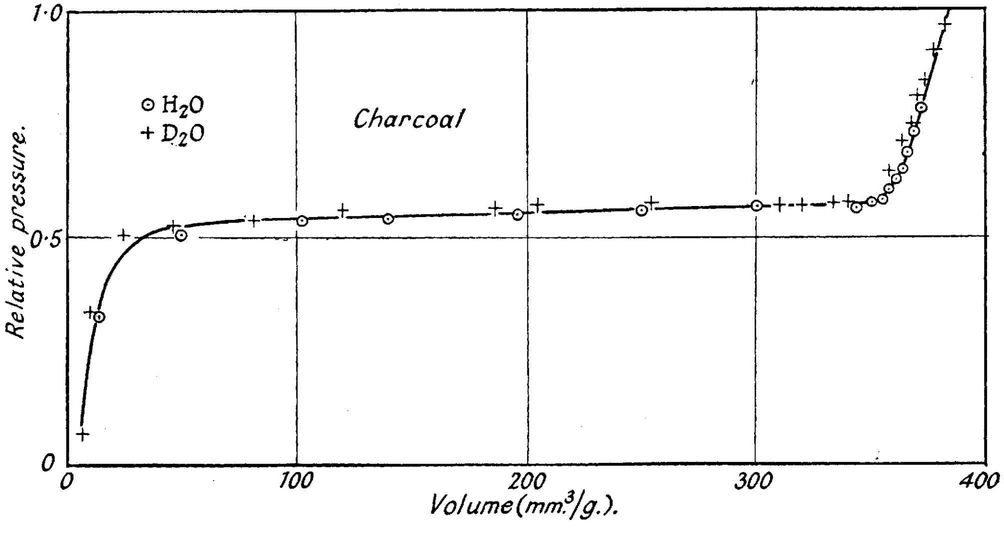


FIG. 3.



EXPERIMENTAL.

The silica gel used was the " Gel B " described by Foster (*Proc. Roy. Soc.*, 1934, *A*, **146**, 129), and the ferric oxide gel that used for the alcohol isothermals (Foster, *ibid.*, **147**, 128). The charcoal was the specially purified sample of Dorsite described as " Charcoal C " by Allmand, Hand, and Manning (*J. Physical Chem.*, 1929, **33**, 1710). Over the manometric range the pressure-change method was used in order to obtain as large a number of experimental points as possible. All the isothermals described are " descending " curves obtained by withdrawal of water vapour from the fully saturated adsorbent. No " ascending " curves were determined, since the hysteresis phenomena have already been studied in detail by Lambert and Foster (*loc. cit.*). The vapour pressure of the sample of heavy water used (99·2%) was 20·76 mm. at 25° (Lewis and Macdonald, *loc. cit.*, give 20·78 mm.). Since the low-pressure measurements require accurate vapour-pressure data for the calibration of the Pirani gauge, the vapour-pressure curve of solid deuterium oxide was determined down to − 23°, where the vapour pressure was 0·51 mm. The best curve through the experimental points gave the relation $\log_{10} p = 9{\cdot}985 - 2577/T$. The general procedure was to obtain a reproducible isothermal with ordinary water, then to remove as much of this as possible by evacuation at the usual temperature of activation of the adsorbent, which was then charged with heavy water. After the first desorption run, the liquid removed from the gel was rejected, and a fresh sample of heavy water used for the second run. Finally, the water isothermal was redetermined in order to make certain that no shift of the isothermal had occurred.

DISCUSSION.

The formation of the unimolecular layer takes place according to the well-known Langmuir equation, $c = zbp/(1 + bp)$, where z is the saturation value and b a constant, c being the concentration in the adsorbed layer at pressure p. If this is written in the form $p/c = 1/zb + p/z$ we see that p/c is a linear function of p, and the slope of the line should be $1/z$, whence the saturation value can be found. In Fig. 5 the low-pressure points for ferric oxide are plotted in this way and found to follow the relation $p/c = 0{\cdot}016 + 0{\cdot}455p$, whence $1/z = 0{\cdot}455$ or $z = 2{\cdot}2$ millimols. or 40 mg. of water per g. of gel. Since the hysteresis phenomena associated with capillary condensation do not appear until a concentration of about 120 mg./g. is reached, it seems likely that the adsorbed layer is about 3 molecules thick when condensation begins. In the region of capillary condensation represented by the flat portions of the curves of Figs. 1 and 2, the points for heavy and light water are seen to fall closely on identical curves. In Fig. 6, where the data for silica gel are plotted as radius–volume curves (calculated from the Kelvin equation), it can be seen that the points for the two liquids fall on the same curve, as predicted by the capillary theory.

FIG. 4.

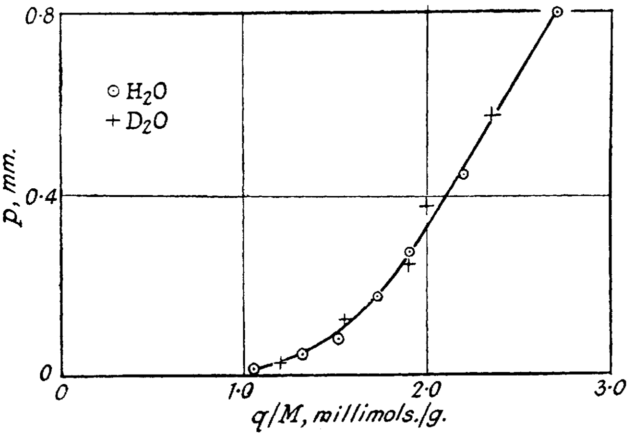


FIG. 5.

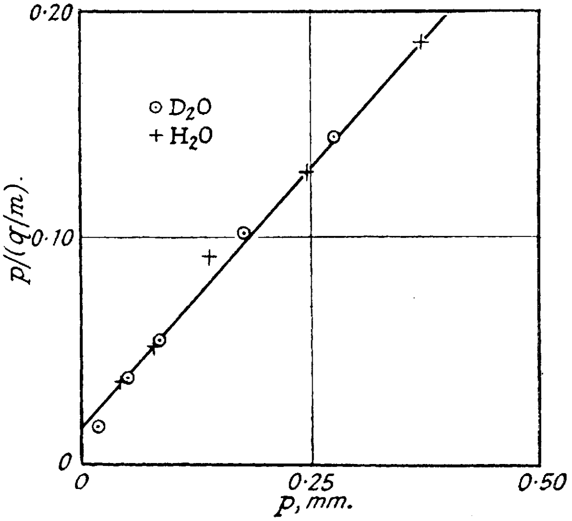
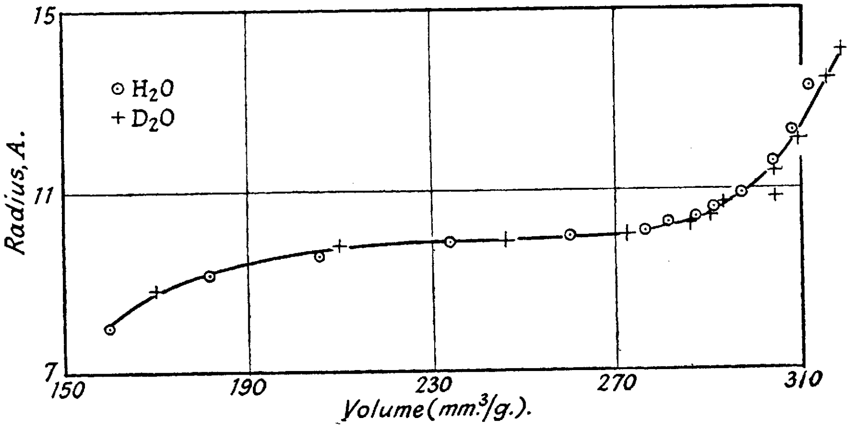


FIG. 6.



The points for heavy water on charcoal, Fig. 3, appear to lie very slightly above those for ordinary water, and a close examination of the data in the region of $V = 300$ mm.^{3}/g. suggests that the former is held at a relative pressure some 3% higher than the latter, whereas King and Lawson (*loc. cit.*) found a difference of the order 5% in the opposite direction. Comparison of Fig. 3 with Figs. 1 and 2 shows that the real anomaly in the behaviour of charcoal is that scarcely any adsorption takes place at low pressures before the flat part of the isothermal is reached. This would appear to indicate that no layer adsorption precedes the capillary condensation process. The pressure at which the isothermal flattens out is roughly the same as with ferric oxide gel, but the latter is then already holding enough water to form a layer 2 or 3 molecules thick before condensation begins. Now, it has been pointed out by Polanyi (*Trans. Faraday Soc.*, 1932, **28**, 316) that capillary condensation is essentially a secondary process and will not take place before the surface of the adsorbent is covered with a layer at least one molecule thick. Many workers have noticed anomalies in the heat of sorption of water on charcoals; *e.g.*, Coolidge (*J. Amer. Chem. Soc.*, 1927, **49**, 712) reported negative values, and Allmand, Hand, Manning, and Shiels (*J. Physical Chem.*, 1929, **33**, 1682) found zero values for the net heat of sorption. Another remarkable fact is that even when liquid water is present in the container, the charcoal does not appear to be wetted by it. There is thus little doubt that the adsorptive force between the charcoal surface and the water molecules is abnormally small and probably does not suffice to overcome the cohesive forces between the water molecules, which therefore tend to remain together in bulk rather than to spread over the surface. Fowler ("Statistical Mechanics," 2nd edtn., p. 838) has discussed adsorption isothermals where there is an attractive force between neighbouring adsorbed atoms, and also the critical phenomena observed in the condensation of metal vapours on solid surfaces. Below a certain critical temperature each isotherm has an unstable region where, at constant pressure, the amount adsorbed increases abruptly from a small to a large value. There is, of course, no actual discontinuity in the water–charcoal isothermals, but the possibility that their shape is due to similar causes cannot be ruled out. Although the capillary hypothesis fits the silica and ferric oxide gel results adequately, one cannot infer an exactly similar mechanism for sorption on charcoal. It is quite conceivable that some sort of critical condensation process as described by Fowler might mask a true capillary condensation process; *e.g.*, the pressure at which the latter would occur if the surface were covered with an adsorbed layer may lie above the critical pressure which must prevail before this layer can be formed. In this case, although the pores would eventually be filled with liquid, the Kelvin equation could not be applied to calculate the radius.

The following argument suggests that these conditions are actually realised in the water–charcoal system. The point of inflexion on the flat part of the charcoal isothermal occurs at practically the same relative pressure (0·56) as that on the ferric oxide isothermal. Thus the most probable pore radius is the same for both adsorbents, *viz.*, 18 A. approx., calculated from the Kelvin equation. Now, so far as is known, all liquids adsorbed on ferric oxide show evidence of capillary condensation, giving isothermals of the same shape as water, whereas no other liquid gives the same type of curve as water on charcoal. An isothermal for ethyl alcohol was determined on the charcoal immediately after the experiments with water. Up to a relative pressure of 0·6 this was found to follow the Langmuir relation $p/c = 0{\cdot}003 + 0{\cdot}0031p$, according to which the unimolecular layer is saturated at 1/0·0031 or 320 mg./g. At this concentration the isothermal is rising almost vertically, so there can be little doubt that the unimolecular layer completely accounts for the total sorption. Evidence has already been presented to show that about 50 mg./g. of alcohol are needed to complete the first layer on ferric oxide gel (*Proc. Roy. Soc.*, 1934, *A*, **147**, 136; this vol., p. 360) and that condensation does not follow immediately, but only after another layer has been adsorbed. On silica gel B, with a calculated pore radius of only 10 A., the sorption of alcohol follows a similar course, with evidence of further layer adsorption and condensation. The fact that these processes are absent on charcoal can have only the obvious interpretation, *viz.*, that there is no room for them to take place, *i.e.*, the unimolecular layer completely fills the pores. If this is true, however, it follows that our calculated pore radius is incorrect and the true value is not 18 A. but probably between 5 and 10 A. If it were actually as high as 10 A. we might expect the alcohol isothermal to resemble that on silica gel, whereas in fact it does not show the linear middle portion characteristic of this gel but resembles those of the slightly larger molecules described in the preceding paper, which arise when "persorption" occurs. Even if we assume a radius as high as 10 A. we should then expect condensation to occur at the same relative pressure as on silica gel (0·35) instead of at the observed value of 0·56. It therefore seems likely that on charcoal, the condensation which would occur at or below 0·35 if the first layer were completed, cannot in practice take place until the relative pressure is raised to 0·56 to enable this layer to be formed. Thus the critical pressure which must prevail before condensation begins is characteristic, not of the condensation process, but of the layer adsorption process. A similar contrast in the behaviour of water and carbon disulphide on charcoal is discussed by Brunauer ("Physical Adsorption of Gases and Vapours," Oxford, 1944, p. 175), who suggests two alternative explanations in terms of dipole attraction between water molecules.

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[*Received, January 24th,* 1945.]