The Production of Active Solids by Thermal Decomposition. Part IV. Vermiculite.*

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The effect of heat on both natural ("magnesium") (I) and barium-exchanged (II) vermiculite has been examined by subjecting them to a steadily rising temperature on the electrical sorption balance *in vacuo* (I and II) and on a conventional thermal balance "in air" (I only); simultaneous readings of weight loss w, time t, and temperature T were taken, and the quantity $\Delta w/\Delta T$ was plotted against T. The resultant curves (which are somewhat analogous to those of differential thermal analysis) show significant differences between magnesium and barium vermiculite *in vacuo*, and between the vacuum and air experiments for magnesium vermiculite itself.

The thermal "activation" of the natural vermiculite has been studied (i) by heating separate samples for 6 hr. *in vacuo* at a succession of fixed temperatures and measuring the specific surface by sorption of nitrogen and of oxygen, and the apparent density in a number of liquids; and (ii) by heating the same sample at a succession of fixed temperatures T *in vacuo* on a sorption balance, cooling to 25°, and then determining the sorption isotherms of carbon tetrachloride and of water vapour. The specific surface increases fairly steadily over the whole range of temperature and the apparent density varies in a manner which indicates the presence of holes of a molecular size in the products formed at higher temperatures. All the water lost on heating at temperature T can be resorbed on cooling, provided T does not exceed 480° C or so.

The process of exfoliation has been studied with the aid of surface-area measurements; and it has also been shown possible to reduce the specific surface of the exfoliated material by about one-third by squeezing—an example of the adhesion of surfaces at room temperature without the use of high pressures.

On exchange of the Mg^{++} for Ba^{++} ions the vermiculite behaves differently towards water, which is now taken up in two stages.

Vermiculite is a silicate mineral resembling mica both in appearance and in its layer structure (see Grim, "Clay Mineralogy," McGraw-Hill, New York, 1953, p. 72). On gradual heating it loses a considerable amount of water over a wide range of temperature; but if it is "shock-heated" by plunging it into a furnace at, say, 950°, the sudden expulsion of water causes the material to swell greatly, and results in "exfoliated" vermiculite. The quantity of water lost, and the power of exfoliation, can be greatly modified by substituting the exchangeable Mg^{++} ions of the natural substance by various other ions. The specific surface of the exfoliated material as measured by gas sorption (Harris, *J. Amer. Chem. Soc.*, 1949, **71**, 363) is known to be several times greater than that of the unheated material, and the substance clearly offers an interesting example of a solid rendered "active" by heating; it was accordingly considered worth while to carry out a more detailed investigation of the effect of heat on the substance, somewhat along the lines of earlier studies (cf. Parts II and III, *locc. cit.*).

Materials.—The vermiculite was from South Africa, its exchangeable cation being largely Mg^{++}. The analysis [kindly supplied by Vermiculite (London) Ltd.] was SiO_2, 39·37; TiO_2, 1·25; Al_2O_3, 12·8; Fe_2O_3, 5·45; FeO, 1·17; MgO, 23·37; CaO, 1·46; Na_2O, 0·80; K_2O, 2·46; H_2O, 11·09; CO_2, 0·60; P_2O_5, 0·15; BaO, 0·04; MnO, 0·30; S, 0·14%.

It was in the form of plates *ca.* 1 cm. by 0·5 cm., and before use was ground in a hand-operated coffee mill and sieved, the fraction $-40 + 20$ mesh being used for all experiments. To prepare the "barium" vermiculite, Barshad's procedure was adopted (*Amer. Min.*, 1949, **34**, 675; 1950, **35**, 225; 1948, **33**, 655).

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* Parts II and III, *J.*, 1953, 3945, 3951.

EXPERIMENTAL

Both the untreated and the " barium " vermiculite were first submitted to thermogravimetric analysis *in vacuo*, with the aid of an electrical sorption balance (Gregg, *J.*, **1946**, 561; Gregg and Sing, *J. Phys. Coll. Chem.*, 1951, **55**, 597). With the pumps running, the temperature of the sample was raised at a uniform rate of 3·5°/min. by means of an external furnace regulated by hand, and readings of weight, time, and temperature (on a resistance thermometer buried in the sample) were taken at frequent intervals. The original vermiculite was similarly analysed " in air " on the open thermal balance (cf. Gregg and Winsor, *Analyst*, 1945, **70**, 336). The results are best represented by plotting $\Delta w/\Delta T$—the average fractional rate of loss of weight per degree, over a short interval of temperature—against temperature T, curves somewhat analogous to those of differential thermal analysis being then obtained.

Next, one and the same batch of the untreated material was heated *in vacuo* on the sorption balance, at each of a succession of fixed temperatures within the range 20—800°, till no further loss in weight occurred. The sorption isotherm of carbon tetrachloride was then measured at 25° to find the specific surface, followed, after outgassing at 25°, by the sorption isotherm of water vapour; the sample remained *in situ* on the balance throughout.

In a further set of experiments *separate* samples of the untreated vermiculite were heated for 6 hr., each at a different fixed temperature, the specific surface of the products being then determined by sorption of nitrogen and of oxygen at −183° (see Gregg and Stephens, *J.*, **1953**, 3952, for apparatus). A second set of samples was similarly prepared, and their density determined by immersion in water, in carbon tetrachloride, in decalin (cf. Gregg and Sing, *J. Phys. Coll. Chem.*, 1952, **56**, 388), and sometimes in helium by using the volumetric sorption apparatus mentioned below. At the higher temperatures (above 300° for sorption and above 400° for density) the sample was prepared " in air " on the open thermal balance and then transferred to the container bulb of the apparatus, where it was outgassed for 1 hr. at 20°; but at the lower temperatures the sample was prepared in the bulb by heating it there for 6 hr. under vacuum.

The process of exfoliation was now studied by shock-heating separate samples of the untreated material for 5 min. in a furnace at 650°, 750°, and 950°, severally, and determining the specific surface by means of oxygen sorption. Then, in an attempt to discover how far the accessible surface could be reduced by mechanical pressure the sorption isotherm of carbon tetrachloride at 25° was measured on the 950°-sample both before and after squeezing: by laying the individual pieces (5000 in all) between two boards, and loading the upper one with weights, it was possible to reduce the average thickness 20-fold.

With the barium-exchanged material only two sets of experiments were carried out, *viz.*, thermogravimetric analysis and measurement of the resorption of water on a sample calcined for 4 hr. *in vacuo* at 150°.

RESULTS AND DISCUSSION

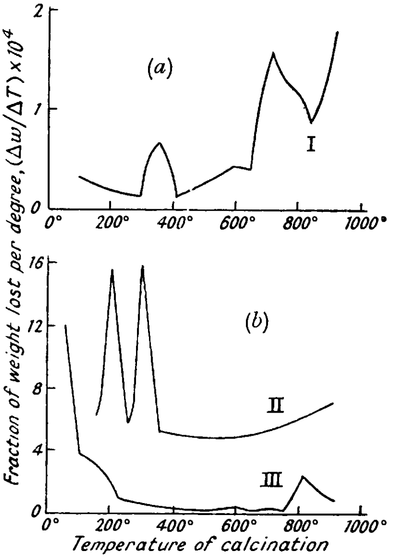
The curve of $\Delta w/\Delta T$ against T, obtained by thermogravimetric analysis of the untreated material, is given in Fig. 1*b*: the peaks at *ca.* 200° and *ca.* 300° " in air " (curve II) agree reasonably with the endothermic peaks, at *ca.* 180° and *ca.* 280°, respectively, obtained in Barshad's differential thermal analysis (*loc. cit.*), and the further slow rise between 600° and 900° shows some correspondence with Barshad's endothermic peak rising from 720° to a maximum at 800°. The curve " *in vacuo* " (curve III) is quite different, showing as it does an almost continuous fall from 50° to 220°. The loss at temperatures below 500°, both in air and *in vacuo*, almost certainly represents molecular rather than structural water, since it is reversible (see later); but at the same time the water cannot *all* be held by van der Waals forces, otherwise it could scarcely require temperatures of 220° in a vacuum or 300° in air for its expulsion; but whether it consists of water of hydration (Hofman and Hausdorf, *Z. Krist.*, 1942, **104**, 265) or merely of specially oriented molecules (cf. Hendricks and Jefferson, *Amer. Min.*, 1938, **23**, 863), or is bound in some other manner, cannot be decided from the present data.

The sorption isotherms of nitrogen and of oxygen are of Type II (B.E.T. classification) so that the specific surface is readily calculated from them (*J. Amer. Chem. Soc.*, 1938, **60**, 309) and is plotted against the temperature of calcination in Fig. 2*b* (curve III and IV).

The sorption isotherms of carbon tetrachloride are likewise of Type II (except for the

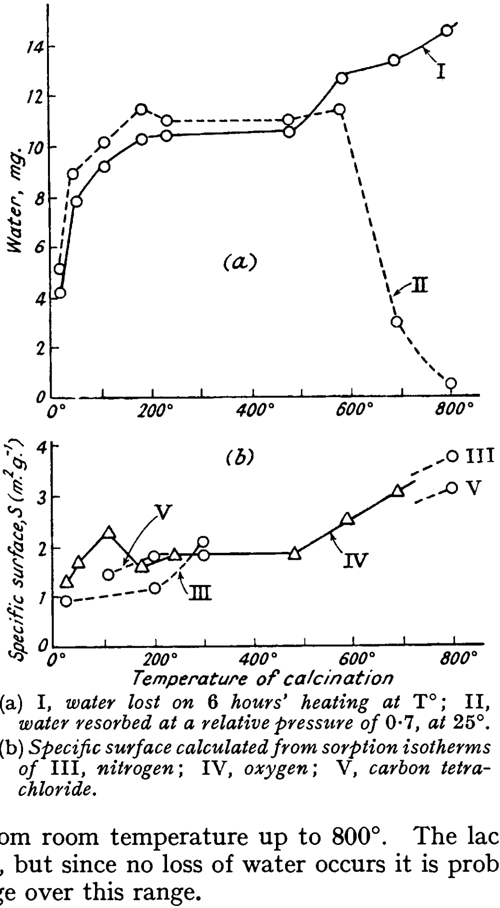
800° sample) but there is no sharp knee, so that, because of the low value of the B.E.T. *c*, the specific surface cannot be calculated by the ordinary B.E.T. procedure. Instead, it has been assumed (Gregg and Hill, to be published) that the monolayer is complete at or near the point where $p/p_0 = 0{\cdot}5$, and the uptake at this pressure, say $x_{0\cdot5}$, has been taken as proportional to specific surface in Fig. 2, curve V. As will be seen, $x_{0\cdot5}$ rises sharply from 500° or so upwards, *i.e.*, as the structural water is lost. The finer details of the curve at low temperatures are more doubtful, but combination of the carbon tetrachloride data with those from oxygen and nitrogen sorption leaves little doubt that the specific surface rises fairly steadily from room temperature up to 800°. The lack of data between 300° and 500° is regrettable, but since no loss of water occurs it is probable that the specific surface shows little change over this range.

FIG. 1. *Thermogravimetric analysis of* (a) *" barium " vermiculite,* (b) *" magnesium " vermiculite.*



I, III, in vacuo; II, *in air. Plot of* Δw/ΔT *against the temperature of calcination* T. (Δw = *fractional change in weight in the temperature interval* ΔT.)

FIG. 2. *Heat treatment of magnesium vermiculite. Various quantities plotted against temperature of calcination* T.



(a) I, *water lost on* 6 *hours' heating at* T°; II, *water resorbed at a relative pressure of* 0·7, *at* 25°.

(b) *Specific surface calculated from sorption isotherms of* III, *nitrogen*; IV, *oxygen*; V, *carbon tetrachloride.*

The results for density (see Table) give information as to pore size (cf., *e.g.*, Franklin, *Trans. Faraday Soc.*, 1949, **45**, 274). Those measured in helium should be nearest to the

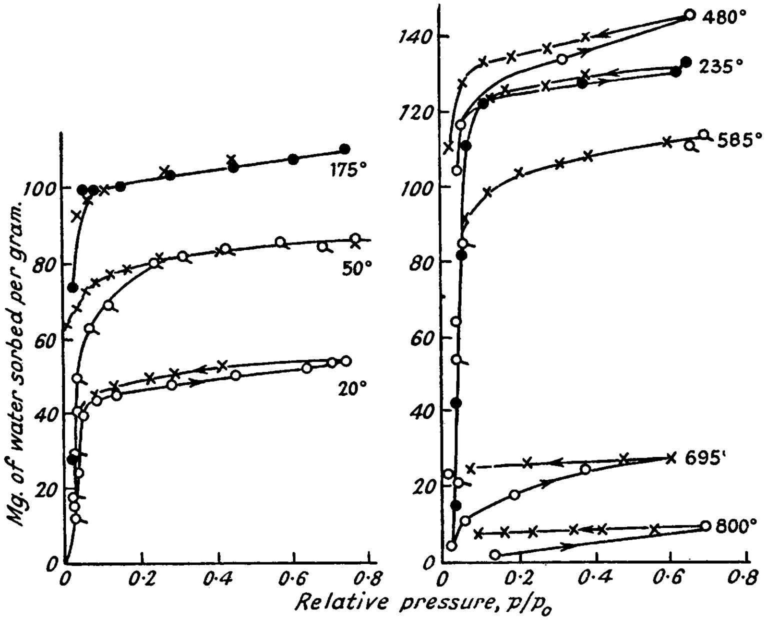
Density (*g. cm.*$^{-3}$) *of vermiculite calcined at various temperatures,* T°, *for* 6 *hours.*

	Density in					Density in			
T°	H_2O	CCl_4	He	$C_{10}H_{18}$ ‡	*T*°	H_2O	CCl_4	He	$C_{10}H_{18}$ ‡
20 *	2·46	2·33	2·37	—	400 †	2·7	2·56	—	—
50 *	2·5	2·4	—	2·49	500 †	2·80	1·90	—	—
108 *	2·77	2·54	2·56	—	600 †	2·86	1·93	—	1·62
164 *	—	2·62	—	2·22	700 †	2·83	2·37	2·7	1·62
214 *	2·81	2·62	2·58	—	800 †	2·37	2·37	—	1·77
304 *	2·88	2·67	2·71	2·23					

* Prepared in vacuum. † Prepared " in air." ‡ $C_{10}H_{18}$ = Decalin.

true density but high precision is difficult to attain; the density in carbon tetrachloride is approximately the same as in helium for temperatures up to 300°, and falls below it from 400° upwards, whilst the density in decalin lies below both the helium and the carbon tetrachloride value from 164° upwards. Presumably, then, there are (*a*) above 400° holes large enough to admit helium and too small to admit carbon tetrachloride molecules, and (*b*) above 164° further holes large enough to admit carbon tetrachloride (and helium) but too small to admit decalin molecules. From the difference in densities the volume (per g. of solid) of holes of type (*a*) is calculated for the 700° sample to be 0·054 cm.^{3} and of type (*b*) 0·137 cm.^{3}. In water the density increases fairly continuously up to 700° and it is consistently higher than that in any of the other three fluids; this can scarcely be due to a penetration effect, for any holes large enough to admit water molecules should also admit the smaller helium molecules; and it probably signifies an increase in the density of the water in the interfacial layer owing to the strong interaction, already referred to, between the water and the solid.

FIG. 3. *Sorption isotherms of water vapour at* 25° *on a sample of magnesium vermiculite heated* in vacuo *at a succession of fixed temperatures* T *for* 6 *hours. The temperature* T *is marked on each isotherm.*



Circles represent adsorption, *crosses* desorption, *measurements. The curve for* 113° *is omitted as it is very close to that for* 175°. *The isotherm for* T = 20° *was measured at* 20°.

The adsorption isotherms for water vapour (Fig. 3) were of Langmuir type up to the highest pressure studied (usually $0{\cdot}7p_0$); one isotherm, that on the 175° sample, was carried up to saturated vapour pressure and it still remained almost of Langmuir type, though with a slight but significant upward bend between relative pressures of 0·7 and 1·0. Hysteresis was particularly marked with the samples calcined at 695° and 800°; and since the time for equilibration steadily increased from *ca.* 10—15 min. for the 110° sample up to several hours for the 800° sample, the hysteresis is probably due, in part at least, to penetration effects.

In Fig. 2*a* the data for weight lost on calcination due to release of water (w_c, curve I) are compared with those for the weight (w_x, curve II) taken up again at a relative pressure of 0·7, which is situated on the flat portion of the isotherm. As will be seen, the two quantities do not differ greatly for any one temperature of calcination, so long as this is below 480°. Since w_c is calculated from the initial weight of the air-dried sample, which is somewhat dependent on the relative humidity of the atmosphere, exact agreement between w_c and w_x is not to be expected; and it is fair to infer that the loss of water below 480° or so is completely reversible, whereas at 695°, and still more at 800°, the lattice structure is changed in such a way that most of the lost water cannot be taken up again (cf. Grim, *op. cit.*, p. 74). It should be noted that w_x (or w_c) is far greater than would correspond to a completed monolayer of water molecules adsorbed on the specific surface S : *e.g.*, for the 200° sample this would be only 0·5 mg. or so of water, whereas w_c is *ca.* 103 mg. per g. Thus the resorbed water can reach places inaccessible to nitrogen, no doubt because it can cause the solid to swell (cf. Walker, *Nature*, 1949, **163**, 726).

In one experiment the form of the sorption isotherm in the region near saturation was studied in detail: a 10-g. sample of untreated vermiculite was outgassed at 50° on the sorption balance, to a loss of 8·4% by weight, and the water sorption isotherm measured with the thermostat bath at 15°, *i.e.*, *ca.* 10° below the temperature of the room. Even when the pressure had reached the saturated vapour pressure for 15°, the uptake showed no marked increase, so condensation to bulk liquid had certainly not occurred; nor did it occur when the vapour became supersaturated by allowing the bath to rise to some 3° higher than the temperature of the sample, as measured on the resistance thermometer.

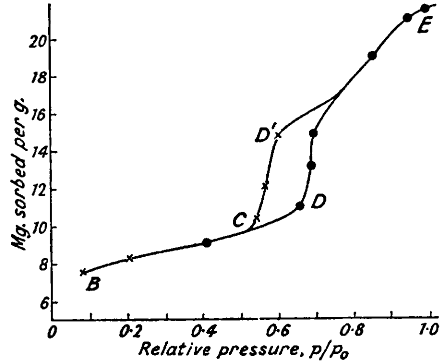


FIG. 4. *Sorption isotherms of water vapour on barium vermiculite at* 15°. *Circles represent* adsorption, *crosses* desorption, *measurements.* (p = *equilibrium pressure*; p_0 = *saturated vapour pressure at* 15°.)

This failure of a supersaturated vapour to condense as bulk liquid on to a porous solid—which implies that there would be a finite contact angle between the adsorbed film and the bulk liquid, corresponding to a difference in entropy between the two states—is of more common occurrence than is usually supposed.

Barium-saturated Vermiculite.—The curve of $\Delta w/\Delta T$ against T for the " barium " vermiculite *in vacuo* (Fig. 1*a*) differs markedly from that for the untreated material both *in vacuo* and in air (Fig. 1*b*). Peaks are now situated at about 360° and 700°, and moreover the *total* loss of water is only 12·7% as compared with 21·3% for the magnesium vermiculite. The shift in, and the lowering of, the high-temperature peak implies that the ion exchange has affected not only the water of " hydration " but the structural water also.

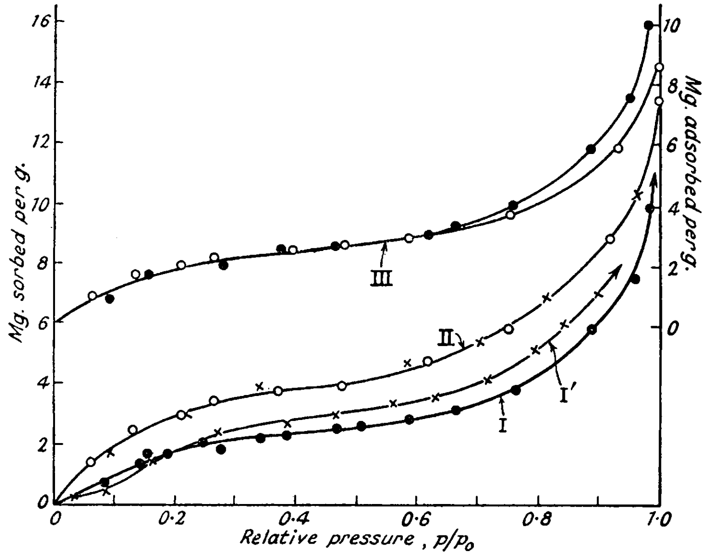
Fig. 4 shows the sorption isotherm of water vapour on a sample of the barium vermiculite which had been heated for 4 hr. *in vacuo* at 150°; *two* distinct steps, *BC* and *CDED′* are now present, the latter comprising a hysteresis loop and, whereas the amount sorbed along *BC* is still fairly close to that lost (*viz.* 7·2%) on the initial calcination *in vacuo*, at *E* it is more than twice this amount.

Comparison with Walker's *X*-ray data (see " X-Ray Identification and Structure of the Clay Minerals," Min. Soc. Monograph, 1951, pp. 199—223) suggests that the two steps correspond respectively to one and two molecular layers of water interleaved between aluminosilicate layers. Walker found for the *c*-spacing of barium-vermiculite 12·3 Å if air-dried, 15·7 Å if wet, and 9·26 Å after heating to 700°; hence the increase in *c*-spacing brought about by the water is 3·04 Å in air-dried and 6·4 Å in the wet material, values close to those expected for one and two molecular layers of water respectively. If

" air-dried " be taken as implying a relative humidity of 40—60%, then the 3·04 Å layer corresponds to the region near *C* of Fig. 4, and the 6·4 Å layer to *E*. The hysteresis loop is probably associated with strains produced in the solid by the swelling (cf. Hirst, *Discuss. Faraday Soc.*, 1948, **3**, 22).

Exfoliation.—The specific surface of the exfoliated product (measured by oxygen sorption) was found to be 2·5, 4·2, and 10·1 m.^{2} g.$^{-1}$ for the temperatures 650°, 750°, and 950° respectively. These areas are far less than the area which would be produced if every aluminosilicate layer were accessible to the oxygen; for, if it is assumed that the thickness of each such layer is 9·26 Å and its density 2·13 g. cm.$^{-3}$, the " theoretical " area would be $2/10^4(2{\cdot}13 \times 9{\cdot}26 \times 10^{-8})$, *i.e.*, 1030 m.^{2} g.$^{-1}$. It thus appears that only a small fraction of the total number of layers is exposed, the average number *n* of layers per " micelle " of exfoliated solid being 410 at 650°, 240 at 750°, and 100 at 950°. (For the original vermiculite n = 1140 layers, corresponding to a thickness of *ca.* 11 μ per micelle, compared with the average geometrical thickness of the flakes, *viz.*, *ca.* 250 μ. Thus even the original material possesses an appreciable " internal " surface.)

FIG. 5. *Sorption isotherms of carbon tetrachloride vapour on exfoliated vermiculite at* 15°, *before and after squeezing.*



I, I′, *After squeezing*; II, *before squeezing*; III, *superposition of isotherms. The solid circles represent a simple re-plot of* I; *for the open circles the ordinates of* II *have been divided by* 1·6. *Circles represent* adsorption, *crosses* desorption, *measurements. For curves* I *and* II *use left-hand scale, for curve* III *use right-hand scale of ordinates.*

From these data, two possible mechanisms for exfoliation suggest themselves. (*a*) The steam, suddenly liberated between each pair of aluminosilicate layers, forces the layers apart in virtue of its high pressure, so that, for a moment, the full theoretical surface is exposed; but the surface immediately begins to decrease again by sintering (cf. Part I, *J.*, 1953, 3940). (*b*) The steam does not necessarily escape to the exterior along the interplanar channels in which it is liberated, but may find its way into neighbouring channels through cracks *across* the planes until it has accumulated sufficiently in certain channels (actually $1/n$ of the total number of interplanar spaces originally present) to prize apart the bordering layers. Of the two mechanisms (*b*) is the more probable, since according to (*a*) the specific surface should *decrease* with increasing temperature owing to increased sintering, whereas in fact it increases.

It would seem that a minute degree of exfoliation occurs even when the material is heated *gradually* as in the earlier experiments; the original material probably contains only a single layer of water molecules between the aluminosilicate planes (cf. Walker, *Nature*, 1949, **163**, 726; 1950, **166**, 695), and if this were expelled without disturbance of the main structure, it would leave a channel only 3·3 Å across, whereas the density data show that for temperatures below 300° there are holes large enough to admit carbon tetrachloride molecules, *i.e.*, with a width of at least 5 Å.

Squeezing the exfoliated material reduced the specific surface (as measured by oxygen sorption) from 10·1 to 5·9 m.^{2} g.$^{-1}$, *i.e.*, nearly half the surface was either sealed off or destroyed by adhesion of neighbouring micelles.

Now the carbon tetrachloride *adsorption* isotherms at 15° on the squeezed and the unsqueezed samples are found to be superposable within experimental limits (below a relative pressure of *ca.* 0·8) if the ordinates of the " unsqueezed " isotherm are divided by 1·6 (Fig. 5). The sorption over this range must therefore consist solely of adsorption on the walls of the pores and not of capillary condensation; for both the pore sizes themselves and the pore-size distribution would obviously be greatly altered by the squeezing, so that if capillary condensation were present, the ratio of sorption on the two samples would vary with pressure. The presence of a hysteresis loop with the squeezed material does not contradict this conclusion; the loop persists down to a relative pressure of less than 0·2 which, as has been shown, corresponds to a still incomplete monolayer, so that it cannot be ascribed to capillary condensation. More probably the hysteresis is due to a swelling effect which by prizing apart some layers opens up new surfaces (cf. Hirst, *loc. cit.*).

From the carbon tetrachloride isotherms, then, one infers that the squeezing has reduced the specific surface by 1·6-fold, in reasonably good agreement with the 1·7-fold (= 10·1/5·9) reduction inferred from the oxygen isotherms.

The process may be likened to a cold-welding, and is facilitated both by the thinness, and consequent deformability, of the laminæ, and also by their favourable orientation towards one another. These factors explain how it is possible so easily to bring about a reduction in specific surface of an order which usually—as in powder metallurgy—requires high pressure combined with elevated temperature.

Conclusion.—The calcination of magnesium vermiculite represents a somewhat unusual example of the thermal activation of a solid inasmuch as the water is gradually driven off, and the specific surface correspondingly gradually increases, over a wide range of temperature, provided the maximum temperature is approached gradually; and in the fact that the water lost at a temperature as high as 480° is completely taken up again on exposure to water vapour at room temperature.

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