peak in the region of 180° C is probably due to amorphous material such as alumina gels, but allophane may also be present. The presence of gibbsite in samples B, C and D and kaolinite in all samples was confirmed by X-ray analysis. Semi-quantitative estimates of gibbsite and kaolinite (Table 1) were obtained from Fig. 1 by reference to a differential thermal trace made by standard kaolinite after allowing for the amount of water lost on heating gibbsite relative to that lost on heating kaolinite.

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Density of Clay–Water Systems

A RECENT paper by Deeds and Van Olphen[1] gives density data for the bentonite–water system which is not in agreement with the results of Anderson and Low[2]. Since the pressure chamber method designed by the latter authors gave promise of being extremely accurate, it seems necessary to re-examine their results.

Anderson's method makes use of the slope of the curve of water content versus volume of the clay–water system. This gives directly the partial specific volume of the water phase, so that changes of slope are interpreted as changes of specific volume. If we plot the deviations of Anderson's points[3] from a straight line, changes of slope can be magnified 100 or more times, allowing a visual estimation of their significance and reliability. When this is done, it is observed that each curve can be considered as a small number of straight line segments, with discontinuities of slope and water content occurring near some of the points at which the mercury capillary was refilled. A sample curve is shown in Fig. 1, and curves of partial density obtained in this way averaged over duplicate sets of results are shown in Fig. 2. (I can supply lists of deviations from straight lines of slope 0·990 for the eight tables of Anderson's thesis. These lists omit the 7 per cent of points containing major misprints. The lines were fitted at water contents between 3·5 and 4·5 gm/gm.)

A general decrease in density is indicated with decreasing water content, but the reliability of the results is obviously low, and detailed comparisons of the four curves are valueless. In addition, the density at high water contents does not agree well with the known density of water, suggesting that the calibration of the capillary or microburette may have been slightly in error.

It is difficult to suggest any sources of inaccuracy in the pressure chamber method which were not carefully investigated by Anderson and Low, and it is especially difficult to understand why refilling the mercury capillary should cause discontinuity of slope as it apparently does.

However, further evidence of inconsistency is obtained if we apply the equation $V = w\bar{v}_w + m\bar{v}_m^3$ to the results. We may use this equation in the form

$$V + \delta = w\bar{v}_w + mv_m + m\left(\frac{\partial V_w}{\partial m}\right)_w$$

where V is the experimentally measured total volume; δ a volume correction constant for each run; w and m are the weights of water and clay respectively in the sample; $\bar{v}_w$ is the partial specific volume of water; v_m the (constant) specific volume of the clay; V_w is the volume of water in the sample.

If the density of the water decreases near the clay surface in the manner of Anderson and Low, the final term must be a small positive quantity which increases with decreasing water content. δ can be evaluated at high water contents, and the other quantities are known. (If the water density is still varying at the highest water contents available, δ will include a small term due to the derivative $\left(\frac{\partial V_w}{\partial m}\right)_w$. This does not affect the argument.)

For every set of experimental results the last term in the equation is negative, and it usually becomes more negative with decreasing water content. Both these results are contrary to expectation; they are not significantly affected by assuming different values of clay or water density within wide limits.
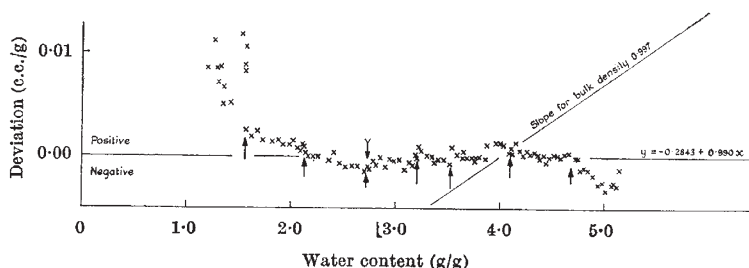

Fig. 1. Deviations of Anderson's Table 9 from a straight line of slope 0·990. Arrows are refilling points. Lithium bentonite at 25° C.
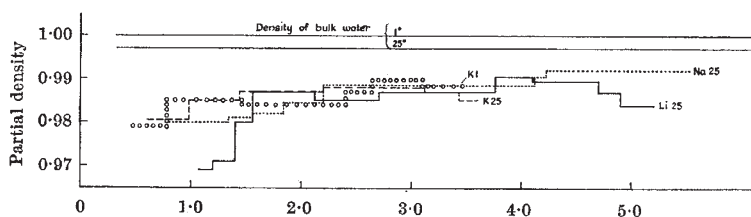

Fig. 2. Average density values from Anderson's data. Lithium, sodium and potassium bentonite at 25° C., potassium bentonite at 1° C.

Until such anomalies are cleared up it must be concluded that variation of the water density at distances greater than a few molecular layers from the clay surface has not yet been demonstrated.

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