

respectively. Apparent porosities for cited weighed oven-dried aggregates are about 10–15 per cent.

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Jan. 26.

- ¹ Mackenzie, R. C., *Nature*, **181**, 334 (1958).
² De Wit, C. T., and Arens, P. L., *Trans. Fourth Int. Congr. Soil Sci.*, Amsterdam, **2**, 59 (1950).
³ Anderson, D. M., and Low, P. F., *Nature*, **180**, 1194 (1957); *Proc. Soil Sci. Soc. Amer.*, **22**, 99 (1958).
⁴ Oakes, D. T., *Proc. Fifth Nat. Conf. on Clays and Clay Minerals*, 46 (*Nat. Acad. Sci.—Nat. Res. Council Pub. No. 556*, 1958).
⁵ Pézerat, H., and Méring, J., *Clay Min. Bull.*, **2**, 156 (1954).
⁶ Bradley, W. F., *Proc. Fourth Nat. Conf. on Clays and Clay Minerals*, 41 (*Nat. Acad. Sci.—Nat. Res. Council Pub. No. 456*, 1956).

DR. BRADLEY has very successfully correlated data from diverse fields of study to show the essential agreement in density determinations on montmorillonite pastes. In this connexion it is interesting to note that early determinations carried out at this Institute, and referred to previously¹, fall quite nicely on the spur of the curve above 77 per cent solids.

In considering the extrapolated part of the curve, however, it must be remembered that montmorillonite oven-dried even at 135° C. (as used by Oakes²) always contains some residual sorbed moisture (the amount may be a few per cent³), and hence it is rather surprising that Dr. Bradley's density value for dry montmorillonite (calculated from X-ray and chemical data) fits the curve so closely. One would have expected some slight discrepancy in view of the fact that the pastes involved were made up with oven-dry montmorillonite. A montmorillonite (Wyoming bentonite) for which we have X-ray and accurate chemical data³ gives a calculated density of 2.78—somewhat lower than Dr. Bradley's value, and the true hypothetical value for 100 per cent oven-dry montmorillonite would be expected to be even lower. The value for dry montmorillonite is somewhat critical in estimating the specific volume of the 'bound' water and, furthermore, it might be remarked that the bulk specific volume of the 'bound' water would be expected to vary with the exchangeable ion and may not be the specific volume of all fractions of this water. One wonders, too, whether it would necessarily be expected that the extrapolated density: montmorillonite-concentration curve need be a smooth continuation of that obtained in the lower concentration regions.

In view of the difficulties in assessment of the final part of the curve (more than 77 per cent solids) there is, to my mind, as yet no unequivocal evidence from density measurements as to the configuration of the first amounts of water sorbed by montmorillonite.

The divergences in discussion mentioned by Dr. Bradley surely arise from the fact that different authors have been considering the interpretation of results from rather different points of view. In the lower solids-concentration region all are agreed that density measurements can give an overall estimate of the density of the water present, the essential accuracy of which is clearly demonstrated by the elegant experiments of Anderson and Low⁴.

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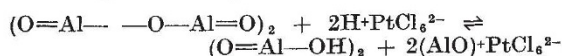
Macaulay Institute for Soil Research,
Craigiebuckler, Aberdeen.

- ¹ Mackenzie, R. C., *Nature*, **181**, 334 (1958).
² Oakes, D. T., *Proc. Fifth Nat. Conf. Clays and Clay Minerals*, 46 (*Nat. Acad. Sci.—Nat. Res. Council Pub. No. 556*, 1958).
³ Mackenzie, R. C., *Silic. Indust.* (in the press).
⁴ Anderson, D. M., and Low, P. F., *Proc. Soil Sci. Soc. Amer.*, **22**, 99 (1958).

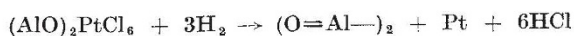
Structure and Mode of Action of the Contact γ -Aluminium Oxide/Platinum

ON the hypothesis of the free-radical structure of heterogeneous catalysts^{1,2}, the mechanism of many catalytic reactions has been deduced in recent years³. In order to explain the action of the γ -aluminium oxide (Al_2O_3)/platinum contact, the structure of the radical $\gamma\text{-Al}_2\text{O}_3$ (ref. 4) as an active transient phase with structural defects should be considered. The model formula of the non-active oxide Al_2O_3 can be represented as follows: $\text{O}=\text{Al}-\text{O}-\text{Al}=\text{O}$. The active $\gamma\text{-Al}_2\text{O}_3$ contains the radicals: $\text{O}=\text{Al}-$ and $- \text{O}-\text{Al}=\text{O}$. Though this formula could be written in several similar forms, because Al_2O_3 is a macromolecular compound, only two types of radical can be expected, namely, $R=\text{Al}-$ (electron donor) and $R-\text{Al}-\text{O}-$ (electron acceptor).

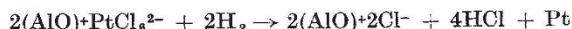
Since the contact γ -aluminium oxide/platinum is obtained as a product of the action of chloroplatinic acid on active γ -aluminium oxide, there is a possibility of exchange between the two compounds, according to the equation:



Under the influence of an excess of chloroplatinic acid, the dissociation of aluminium-platinum compound goes backwards; this can also be explained by the action of the active γ -aluminium oxide as a chromatographic column⁵. In the stream of hydrogen the undissociated $(\text{AlO})_2\text{PtCl}_6$ undergoes reduction as follows:



and as a result of this the radical $\text{O}=\text{Al}-$ appears, which is necessary as an important link in the chain of reactions leading to the hydrogenation of benzene. Thus the active γ -aluminium oxide acquires electron donor properties. But when the concentration of chloroplatinic acid is small, the complete suppression of the dissociation of $2(\text{AlO})+\text{PtCl}_6^{2-}$ is doubtful, this compound being able, under the influence of hydrogen, to retain its ionic form. This checks the regeneration of the primary radical $\text{O}=\text{Al}-$, according to the reaction:



This explains why γ -aluminium oxide/platinum contacts with small contents of platinum lose their activity quickly⁶, because, in my opinion, in the absence of sufficient numbers of $\text{O}=\text{Al}-$ radicals, platinum only activates hydrogen so long as it is saturated with it or with a hydrogen compound (cyclohexane):



But when the radical $\text{O}=\text{Al}-$ appears and co-operates with metallic platinum, then platinum, passing into the atomic state, can also make use of the electrons of $\text{O}=\text{Al}-$ and of molecular hydrogen in turn, so that hydrogen is activated. In consequence of this the hydrogen electron, together with its proton, is as it were thrown aside after the electron arising from the $\text{O}=\text{Al}-$ radical becomes available, and so on in a constantly repeating rhythm⁷. The mechanism of the reaction of hydrogenation of benzene at the γ -aluminium oxide/platinum contact can be represented in the form of a chain reaction, which is accompanied by a migration of electrons⁷.