that recently calculated by Dr Schofield, viz., 4,700,000 sq. cm. per gm. It would appear, therefore, that this method may be capable of giving values of the right order.

From the equation and the $r/W$ curve for a clay, the vapour pressure isotherms at various temperatures can be calculated. These have the usual hyperbolic form with an inflexion corresponding to the break in the $r/W$ curve. Application of the Van't Hoff isochore to the vapour pressure data gives $H$, the total heat of evaporation of water per gm. molecule from the clay at various water contents. It has been found that the values of $H$ obtained from the capillary range of the isotherms fall, when plotted against water content, on rectangular hyperbolae, that for the kaolin having the equation

$$\Delta H - 10,100 = \frac{212}{W^1 - 0.5}$$

where $W^1$ is the water content in gm. per 100 gm. of dry clay.

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THE KINETICS OF CLAY DECOMPOSITION

By P. Murray and J. White.

The use of thermal analysis for the identification of clay minerals differs from its use for the determination of phase transitions in that the latter are, in theory at least, reversible and occur at definite temperatures while the dehydration reactions utilized in the identification of clays are monotropic, irreversible decompositions proceeding at a velocity which increases continuously as the temperature is raised. There is, therefore, no definite transformation temperature and the temperature of the arrest registered on a heating curve depends on the heating rate employed.

In view of the increasing importance of thermal analysis it was decided that an attempt should be made to study the implications of this. An investigation of the kinetics of the dehydration reaction seemed the most obvious approach.

The method adopted was to take continuous weighings with the sample suspended from the pan of a balance in the hot zone of a wire-wound furnace held at constant temperature. Porous alundum crucibles were used to facilitate escape of vapour, the clay being tapped down to minimum volume in the crucible before starting. At the beginning of a run the specimen was suspended in the furnace, at a temperature just below that at which decomposition began, till it was
of constant weight. The temperature was then raised rapidly to the selected reaction temperature, the time at which this was reached being noted, and taken as zero time for the purpose of the run. Weighings were then taken at known intervals throughout the run.

The kinetics of solid reactions are commonly complex due to nucleation, autocatalytic effects, etc., and one of the first objectives was to find whether a simple type of kinetic law enabling a velocity constant to be evaluated was obeyed.

In the present instance the first order law can be written

$$\frac{dl}{dt} = k (l_\infty - l)$$

where $l_\infty$ is the total loss of combined moisture when decomposition is complete and $l$ is the actual loss at time $t$, $k$ being the velocity constant.

On integration this gives

$$\log l - \log l_\infty = -kt.$$  

$l_\infty$ cannot be assumed as known but is got by plotting the logarithms of the amounts decomposed in a constant time interval $\Delta t$ against $t$ the time at the beginning of the interval. If the reaction is monomolecular a straight line will be obtained, from the slope of which $k$ can be got, and thence $l_\infty$ can be evaluated. On applying this treatment to the data obtained for the different clays, it was found that good straight line plots were in fact obtained.

From kinetic theory the relation between $k$, the velocity constant and $T$ the absolute temperature should be of the form $k = Ae^{-E/RT}$ where $A$ is a constant and $E$, the energy of activation per gm. molecule, is obtained from the slope of the log $k$ against $1/T^\circ$A plot which should be linear. Figure 3 shows that this is so for all the clays so far examined. It will be seen that the plots for the kaolinitic clays are practically coincident, with $E$ of the order of 42,000 calories, in spite of the fact that the ball clays would be of much smaller particle size than the kaolins. The sericitic clays give lower values of $E$ but higher values of the velocity constant, and the two plots differ from each other in both slope and position, this possibly reflecting the less definite nature of the clay mineral. The bentonite has a much lower value of $E$ (21,500 cal.) and a lower velocity constant than the others.

To throw light on the variations that occur in thermal analysis the above experiments were repeated using half the quantities of clay used previously. It was found that in all cases higher values of the velocity constant were obtained. The slopes of the log $k$ plots, however, remained approximately the same. For example with Supreme Kaolin while the velocity obtained increased by roughly 25 per cent. the value of $E$ increased only 4 per cent. It would appear, therefore, that the value of $E$ might provide a means of identification which would be relatively little affected by the experimental conditions.

The $k$ values from Figure 3 were used to calculate the amount of reaction per minute throughout the heating range, at various constant
heating rates, using the equation \( \frac{\Delta l}{\Delta t} = k (l_\infty - l) \)

Curves similar in shape to the arrests obtained on a thermal analysis curves were got, the maximum in the case of kaolin occurring at 582°C and 605°C for assumed heating rates of 5 and 10°C per minute respectively. These were considered in reasonable agreement with thermal analysis data.

On repeating the calculations for the case of Wyoming bentonite, the temperatures obtained for the maximum loss per minute were found to be much too high (762°C and 822°C at assumed heating rates of 5 and 10°C per minute), indicating that the reaction constants derived from the isothermal experiments were too small to account for the result of thermal analysis. To investigate this point a weight loss curve was determined for Wyoming bentonite while it was being heated at a constant rate of 8°C per minute. On plotting the decomposition per minute against temperature it was found that the maximum loss per minute now occurred at 735°C indicating a more rapid rate of decomposition than had been indicated by the isothermal experiments. Further, when mean values of \( k \) over successive periods of a minute were calculated, the log \( k \) plot shown by the dashed line of fig. 3 was obtained.

This behaviour of Wyoming bentonite appears, so far, to be unique and is being further investigated. The nature of the mechanism giving rise to the first order reaction curves obtained for it and the other clays is also being studied. The simplest hypothesis is that nucleation, the frequency of which will be governed by a Boltzmann probability factor, is rate-determining. This would be the case (a) if the reaction proceeds entirely by the formation of independent nuclei or (b) if propagation of the reaction from a nucleus proceeds rapidly (relative to the rate of nucleation) up to an upper limiting size of the reacted area.

The above work has been carried out with the aid of grants from the British Iron and Steel Research Association forming part of a programme of work carried out for the Steel Castings Division of that body.

**Discussion on the above two papers.**

Dr Schofield.—I feel sure that the explanation which Dr White gives in the first part is essentially right, and I think it would be interesting if it can be substantiated by calculating the rate of diffusion of the water vapour. Dr Penman of Rothamsted has been successful with carbon disulphide vapour and I think we have the necessary information in the present case at any rate to check the order of magnitude. In the second part he referred to some calculations that I made recently on the basis of negative adsorption of chloride ions taken from some data of Mattson which gave an area of 4-500 sq. cm. per gm. of bentonite. Quite recently Dr Dakshinamurti has done
further experiments and has obtained 800 for a highly purified sample, which is in substantial agreement with the theoretical value, assuming that the montmorillonite is in this suspension completely broken up into sheets. I feel that Dr White can get more solid support from the evidence of X-ray analysis than from these calculations of mine which refer to such different conditions of moisture content.

Dr White.—We were very interested to see that Dr Schofield was here to-day since we had quoted his results in substantiation of our own, and we are particularly grateful to him for his contribution. As comparative newcomers to the field of clay research we have not yet had time to examine the very extensive literature adequately, and we are very glad of his comments.

Added in writing.—With regard to the rate of diffusion of the water vapour we have, in considering the data from the tray experiments with water alone in the trays, arrived at the relationship

\[ t_n = cW \times 1.20 \times 10^{-8} \left( \frac{12}{5} n + \frac{61}{72} - \left( \frac{1}{2} \right)^n \right) \exp \left( \frac{5190}{T_n} \right) \]

where \( t_n \) is the time in hours to dry the \( n \)th tray at temperature \( T_n \), \( W \) the weight of water in each tray initially, and \( c \) a constant equal to 1870, the trays being assumed evenly spaced in the tube. The movement of the step in the clay columns obeys a relationship of the same form, which suggests that a similar mechanism is involved. We have hesitated to accept this finally, however, since an activated diffusion process involving activated jumping of water molecules “held” to the clay surface would lead to a similar law.

With regard to our estimates of the surface areas of the clays, our method is, of course, somewhat empirical, and we were rather gratified to find that the value for Wyoming bentonite calculated by Dr Schofield was of the same order as our own. His comments, however, indicate that the breaking up of the Wyoming bentonite particles was probably not complete in our experiments. This appears to clear up one point which caused us some surprise, that non-swelling Pembina bentonite actually gave a higher value for the surface area than did Wyoming bentonite.