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INTRODUCTION

Knowledge of reactions at solid/liquid and solid/gas interfaces is of great importance in the study of all adsorption phenomena. Techniques that enable a study of molecules (liquid or gaseous) adsorbed onto a surface may be divided into two categories: (a) those that upset the equilibrium between molecules in the gaseous (or liquid) phase above the solid surface and molecules actually adsorbed onto it, and (b) those that do not. Those techniques that do not disturb this equilibrium will give results that would be expected to have greater reliability than those obtained from techniques that upset this equilibrium (for example by heating or by affecting one component of the equilibrium by titration, precipitation etc.)

In an endeavour to study the properties of water adsorbed onto various substances such as clay, wool and textile fibres without affecting the equilibrium the technique of isotopic exchange has been developed. Essentially the procedure is to take a closed adsorber system in equilibrium with a gas (or liquid), part of which is in the sensitive region of a geiger counter, and to add a very small amount of radioactively labelled gas (or liquid) to the system. The adsorber is placed in the bottom of a geiger counter out of the sensitive volume and a known fraction of gas (or liquid) is in the sensitive volume. As the system is at equilibrium there is continuous exchange between the adsorbed molecules on the sample and the molecules in the gaseous (or liquid) state. Thus, when a very small amount, by weight, of the radioactively labelled gas (or liquid) is added to the system, exchange

will take place with the non-radioactive molecules adsorbed on the surface of the material under study. Thus radioactivity will be removed from the sensitive volume of the geiger counter and adsorbed onto the surface of the material, and so the specific activity (count rate), as measured with the geiger counter, will drop. The advantage of this technique is that the equilibrium between the adsorbed molecules and the free gas (or liquid) is not disturbed. The actual amount of radioactive material added is so minute that there is no effective change in the concentration of the free gas (or liquid).

As radioactive exchange takes place with the adsorbed molecules the drop in activity in the sensitive volume of the geiger counter is recorded continuously by plotting the actual count rate on a strip chart recorder.

It can be shown by mathematical analysis that the activity as a function of time consists of a number of logarithmic terms and a constant term. The data obtained from the recorder is taken and a graph of $\log_e$ (specific activity) versus time is prepared. This graph is then resolved into a constant value plus a number of straight lines. The number of straight lines corresponds to the number of different types of water adsorbed onto the surface under study. From the intercepts of these lines with the zero time axis it is possible to calculate the amount of each different type of water present on the surface as a function of the amount of water vapour in the geiger counter (which is known from the volume of the geiger counter and the water vapour pressure.) Also from the slope of these lines it is possible to obtain

the half-time of exchange of each type of water and from this and the intercepts it is possible to calculate the specific rate constant for each type of water. By doing experiments at different temperatures it is possible to calculate the activation energy of each type of water present.

One of the advantages of this technique is that the experiments are carried out at chemical equilibrium and therefore valid thermodynamic data is obtainable. Also the problem of wetting and drying phenomena does not occur. What one is actually studying is the $^3\text{H } ^1\text{H } \text{O}/\text{adsorber}$ system, and not the $\text{H}_2\text{O}/\text{adsorber}$ system but it is unlikely that there would be any qualitative difference between the two systems.

In the present work this technique is used to investigate the clay-water system. An attempt is made to split up the adsorbed water into a number of different types such as exterior surface water, inter-lamellar water and water of hydration of any exchangeable cations present in the clay.

Similar work has been done using Differential Thermal Analysis by Hendricks et. al. ⁽¹⁾ Other attempts using Nuclear Magnetic Resonance ⁽²⁾, ⁽³⁾, ⁽⁴⁾ and Infra Red adsorption ⁽⁵⁾ have not proved very successful because of the complexity of the spectra obtained and the difficulty of distinguishing between the adsorbed water molecules and the structural hydroxyl groupings. Other techniques such as Refractive Index studies ⁽⁶⁾ and the use of heavy water (D_2O) ⁽⁷⁾ have not yielded any information about the different types of water present in clay structures. X-ray diffraction studies, particularly those of Nagelschmidt ⁽⁸⁾ and of

Hofmann and Bilke⁽⁹⁾, while giving confirmatory evidence for some of the deductions made in the present work, do not of themselves give information about the different types of water present such as cationic water of hydration, but only about the total spacings in clay structures.

The disadvantage of Differential Thermal Analysis is that not only are all measurements made at elevated temperatures but also it is a non-equilibrium process and so the results do not necessarily represent a true picture of the clay sample at room temperature. The present technique of radioactive exchange at equilibrium overcomes this difficulty as would techniques such as Nuclear Magnetic Resonance and Infra Red adsorption if satisfactory results could be obtained.

Hendricks et. al.⁽¹⁾ made a study of Montmorillonite using different cationic substituents. They examined the various clays saturated with water from 5% up to 90% relative humidity by Differential Thermal Analysis and then analysed the low temperature endothermic region into components. From their work they concluded that the water on Montmorillonite consists of a single layer of water molecules except where there are cations (which are present to balance the excess negative charge of the Montmorillonite). These cations may or may not be hydrated. Hendricks et. al. found that Lithium and the Alkaline earths Magnesium, Calcium, Strontium and Barium were hydrated, whereas Hydrogen, Sodium, Potassium and Caesium were not hydrated. More recently Ganguly and Gupta⁽¹⁰⁾ have come to the conclusion, from studies based on moisture determinations, chemical analyses and base exchange measurements, that all exchangeable cations including Hydrogen in oven-

dry clay minerals are present in hydrated form. According to Hendricks et. al. as the relative humidity is increased a second layer of water molecules appears on top of the first layer, first appearing, usually, after about 25% relative humidity. Further evidence for this is given by the increase in apparent cleavage spacing of the silicate layers up to about $15.0 - 16.0 \text{ \AA}$ as the relative humidity is increased. At very high relative humidities (about 90%) there would appear, from the Differential Thermal Analysis graphs, to be a further increase in water sorption, but this does not change the apparent cleavage spacings. However according to Nagelschmidt ⁽⁸⁾ and Hofmann and Bilke ⁽⁹⁾ the cleavage spacing does increase considerably above 90% relative humidity to an eventual value corresponding to four layers of water between the silicate sheets of the Montmorillonite. The latter view agrees better with the amount of water detected at these relative humidities in the present work.

In the present work studies have been carried out on the Montmorillonite-water system. The Allophane-water system was also studied briefly. Samples of Potassium Montmorillonite and Hydrogen Montmorillonite were prepared and studied over a range of relative humidities at 0°C . From this data phase diagrams for the two homoionic species were prepared. It was found that there were two different types of water on Hydrogen Montmorillonite at all relative humidities while the Potassium Montmorillonite had two similar types of water associated with it and also a third type which appeared above 80% relative humidity. Both from the absence of a similar third type of water on Hydrogen Montmorillonite at

high relative humidities, and also from the amount believed to be on the Potassium Montmorillonite at 100% relative humidity (calculated by extrapolation) it is thought that this water is associated with the Potassium ions present. X-ray diffraction data for Montmorillonite, as obtained by Nagelschmidt⁽⁸⁾ and Hofmann and Bilke⁽⁹⁾, is considered when assigning the two types of water common to both Hydrogen and Potassium Montmorillonites, and the results reached are in accordance with the basal spacings as given by this data.

Hydrogen Montmorillonite was also studied at temperatures above and below 0°C and from the change in the specific rate constants with temperature the activation energy for each type of water was calculated.

Lithium, Barium and Magnesium Montmorillonites were studied briefly. A third type of water, probably water of hydration of the Lithium ions was detected on the Lithium clay but, at least at 78% relative humidity, there were only two types of water on the Barium and Magnesium clays.

Two samples of Allophane of differing ages were examined and both were found to have two different types of water associated with them at 78% relative humidity. At least one of these types is common to both the samples tested.

PREPARATION OF CLAY SAMPLES

Materials:

1. Ion Exchange Resin

The Ion Exchange Resin used in the preparation of the clay samples was Permutit Ion Exchange Zeo-Karb 225 Hydrogen form cation exchange resin 14-52 mesh. The Ion Exchange resin was backwashed through an ion exchange column to remove impurities. Approximately 2N Hydrochloric Acid (Analar grade) was passed through the resin in the column to ensure it was in the Hydrogen form. Distilled water was then passed down the column until the issuing water was free of all traces of acid, to remove all excess Hydrochloric Acid. The Ion Exchange resin was then stored in distilled water in a stoppered flask until required.

2. Cation Solutions

In order to prepare samples of Montmorillonite saturated with various different cations, solutions of the required cations were prepared. 1 Normal solutions of the cations required were prepared by weighing out suitable amounts of "analar" salts and dissolving them in distilled water. The salts used were: Potassium Chloride; Barium Chloride; Magnesium Chloride and Lithium Sulphate.

3. Clay Samples

All clay samples used in this work were supplied by the courtesy of the Soil Bureau, Department of Scientific and Industrial Research. The Montmorillonite used was a B.P. grade Bentonite which consisted almost completely of Montmorillonite (Soil Bureau Laboratory Number = S680). Two samples of Allophane were used. Allophane B was from

Taupo sandy silt (Parent material Rhyolitic ash). (Laboratory number = SB6673). Allophane A was from Egmont brown loam (parent material Andesitic ash). (Laboratory number = SB6674). The Allophane A sample was derived from volcanic ash of greater age than the Allophane B sample.

Clay Acidity

As both Montmorillonite and Allophane were treated with Hydrogen Ion Exchange resin, their preparation was carried out in acid conditions, and so the pH under which they are prepared will be less than 5. Fieldes and Schofield⁽¹¹⁾ have determined the net electric charge on soil clays at different pH values. Montmorillonite has a net negative charge of 100 milliequivalents per 100 grams clay at pH less than 6, and this corresponds to a negative charge of -0.66 per unit cell. Both the Allophane samples have almost zero charge (actually very slightly positive) at pH less than 5, and thus will effectively have no exchangeable ions associated with them.

A. Montmorillonite

Approximately 0.15 - 0.2 gms montmorillonite were taken and shaken with distilled water to produce a suspension of the clay in water. This suspension was shaken with 2-3 ccs. of Ion Exchange resin and allowed to stand. After the Ion Exchange resin had settled to the bottom of the test-tube containing the mixture, the clay suspension was poured off into another test-tube, and more Ion Exchange resin added. This was shaken and separated as before, and the procedure repeated once more. The clay suspension was then placed in a centrifuge tube and centrifuged. Any impurities and any remaining Ion Exchange resin are deposited on the bottom of the tube in this manner, and the suspension is then poured into another centrifuge tube. One or two drops of the cation solution are then added (in the preparation of hydrogen montmorillonite 1N "Analar" Hydrochloric Acid is used) to flocculate the clay. The solution was centrifuged again, when the clay was deposited. After pouring off the supernatant liquid a few ccs. of the solution of the required cation was added, the clay shaken up with this solution and then recentrifuged.

Two more portions of the cation solution were added to the clay, shaken, and centrifuged. Finally the clay sample was washed in the same manner five times with distilled water to remove any excess cation solution.

After the final washing the clay was made into a slurry with as little water as possible, and this was then poured into a sample tube. The sample tube was a small tube 2-3 inches long with a ground-glass

cone joint at one end for insertion into the bottom of the geiger counter, the other end being sealed.

To remove the water from the sample the tube was attached to a closed system (Figure I). The slurry of clay and water was frozen with liquid air, and the system evacuated. After the slurry had melted the other arm of the system "A" was surrounded with liquid air when the water distilled over into "A".

Figure I

It was found necessary to let the slurry of clay and water melt before lowering the temperature of the arm "A". If this was not done there was a tendency for the partly frozen slurry to jump up and down in the sample tube thus losing clay into the rest of the system.

B. Allophane

As it was not possible to form a suspension of Allophane in water, it was necessary to separate it from the Ion Exchange resin.

in another manner. It was found that the Ion Exchange resin was almost completely held up by fine copper gauze. The resin was first washed well on the copper gauze with distilled water to remove any small particles present. Then portions (2-3 ccs.) of it were mixed with the clay plus a little water and shaken well. After settling the mixture was sieved, and the remaining Ion Exchange resin washed with a little distilled water. The Allophane passed through the gauze because of its small particle size, and after centrifuging the filtrate the supernatant water was discarded, and the process then repeated twice with fresh Ion Exchange resin. The resultant sample was then washed five times with distilled water, after each washing the solution being centrifuged and the supernatant liquid discarded. The clay was then shaken with a little water and poured into a sample tube. After settling, most of the water was poured off, and the remainder removed by drying in a vacuum desiccator over Silica Gel.

At the completion of each experiment about one millilitre of distilled water was added to the sample tube, and the sample was then dried in a vacuum desiccator over Silica Gel. By adding such a large excess of water compared with the amount already on the clay (which would be about 0.01 gm), almost all of the radioactive water ($^3\text{H}^1\text{HO}$) on the clay would be removed. As almost all of the water on the clay, as well as that added, is removed in the vacuum desiccator the dilution of the radioactivity present is well in excess of 100:1.

EQUILIBRATION OF CLAY SAMPLESA. Temperature = 0°C.

The apparatus shown in Plate I is assembled and connected to a two-stage rotary oil pump with ballast by the ground glass joint A. The flask B contains either a saturated salt solution giving the required relative humidity or, for experiments at low relative humidities a solution of concentrated Sulphuric Acid. The flask B is connected through an equilibration arm E to the geiger counter C. This solution is first frozen in liquid air and maintained solid by this means while the whole assembly is evacuated. The stopcock to the vacuum pump is then closed and the solution allowed to melt of its own accord in order to reduce the possibility of cracking the flask as much as possible. In this way most of the dissolved gases in the solution are expelled. The solution is then again frozen in liquid air and the system pumped on by the vacuum pump for some time. This process of removing any dissolved gas (N_2 , O_2 , etc.) which would upset the counting characteristics of the geiger counter is repeated twice more. The vacuum pump is now disconnected from the geiger counter - equilibration flask system. After allowing the frozen solution in B to melt the solution and the clay sample in the sample tube attached to the bottom of the geiger counter (D) are both immersed in an ice-water mixture in Dewar flasks. The system is then left standing in order to reach equilibrium between the clay sample and the solution which determines the relative humidity of the system. Thus, at equilibrium the clay sample will be saturated to a certain

relative humidity, and the amount of water vapour in the geiger counter can be determined, knowing its volume and the saturation vapour pressure at the temperature in question. The solution is kept at this constant temperature for at least thirty-six to forty-eight hours by which time equilibrium will have been established. The total time for the added radioactivity to drop to a steady value is only ten to twelve hours, and by this time the tritiated water vapour has distributed itself in equilibrium proportions between the clay and the geiger counter. Thus the time for establishment of the original equilibrium will be of this order.

B. Other Temperatures

In order to determine the activation energies of the different types of water on hydrogen montmorillonite experiments were performed at -21.3°C and at $+25.0^{\circ}\text{C}$ as well as at 0°C . At both the other temperatures the saturated solutions were degassed and allowed to equilibrate with the clay sample as described in Section A (above). For the experiment at -21.3°C a saturated sodium chloride/ice/water mixture was used which gives this temperature ⁽¹²⁾. In order to ensure that the saturated salt solution did not freeze at this temperature, saturated Calcium Chloride was used (freezing point = -54.9°C ⁽¹³⁾). To make sure that complete equilibration had occurred at this temperature the clay sample and the saturated Calcium Chloride solution were kept at -21.3°C for ten days.

The first experiment at $+25.0^{\circ}\text{C}$ was done in a thermostated room whose temperature was found to be constant to $25.0 \pm 0.1^{\circ}\text{C}$ the temperature being checked at approximately hourly intervals during

a full day. The saturated salt used was Lithium Chloride as this gives a relative humidity of 11.5%, and it was not considered wise to introduce much more water vapour into the geiger counter than this ($0.115 \times 23.576 = 2.71$ mm. Hg.)

As the first experiment at $+25.0^{\circ}\text{C}$ did not give fully satisfactory results it was repeated, but in the second experiment a thermostatically controlled water-bath with a toluene type thermoregulator maintaining the temperature at at least $25.0 \pm 0.05^{\circ}\text{C}$ was used. The sample and the saturated Lithium Chloride solution were equilibrated in the water bath, and then, after addition of counting gas the sample holder was kept in the water bath while counting was being carried out.

PREPARATION OF GEIGER COUNTER
FOR COUNTING

After equilibration is complete the stopcocks on the geiger counter are closed and the saturated salt solution and the equilibration arm E removed. A 20 ml. flask with a ground glass joint on the bottom and a vacuum stopcock and ground glass joint on top (shown attached to geiger counter in Plate III) is attached to the top of the geiger counter, and then the whole apparatus is attached to the vacuum line. The vacuum line is shown in Plate II, but neither of the geiger counters attached to it have a 20 ml. flask attached.

The apparatus is now evacuated as far as the lower stopcock on the geiger counter. After all the air has been pumped out the system is flushed out with counting gas (which is stored in the large inverted flask A) and reevacuated. The stopcock to the vacuum pump is now turned off, and the vacuum line is filled with counting gas to a pressure of about 11 cm. Hg from A, the pressure being measured with a mercury manometer. The stopcock to the geiger counter is now opened and closed rapidly to introduce counting gas into the geiger counter, in order to prevent the water vapour in the geiger counter from diffusing into the rest of the system. More counting gas is let into the vacuum line, the stopcock to the geiger counter opened and closed and so on, until the pressure inside the geiger counter is the same as that in the rest of the vacuum line and is equal to about 10-11 cm. Hg. All the vacuum line except the geiger counter (containing counting gas plus water vapour) is now evacuated. Next tritiated water vapour is introduced

into the space between the two stopcocks on the geiger counter in one of two procedures.

In the majority of experiments, after turning off the stopcock to the vacuum pump, a tube containing tritiated water at room temperature was opened to the vacuum line and tritiated water vapour allowed to diffuse through the system. After about 20 seconds the upper stopcock on the geiger counter is closed, and then the tube containing the tritiated water is immersed in liquid air. By this means all the tritiated water vapour in the system except for that between the two stopcocks on the geiger counter is frozen back into its container. This is then isolated from the rest of the vacuum line and, after removing any remaining gases by pumping on the system, the 20 ml. flask is filled with counting gas at about 1 cm. higher pressure than that in the geiger counter. The geiger counter + 20 ml. flask is now removed from the vacuum line and transferred to the counting apparatus where it is placed inside the lead bricks (see Plate III).

For samples of very low relative humidity, for example concentrated Sulphuric acid solutions with relative humidity $\approx 1\%$, and for the experiments at -21.3°C , as the amount of water vapour in the geiger counter was very small the amount of tritiated water vapour would be comparable to the amount already present. Provided that the relative humidity in the geiger counter was not too low the actual amount of water vapour present would be many times greater than the amount being added (the ratio of the volume of geiger counter to the volume of the space holding tritiated water is greater than 100 to 1). If this was

not so it would be necessary to reduce the actual amount of tritiated water vapour being added. In order to do this a "hotter" sample of tritiated water was used and this was made to fill the space between the upper and lower stopcocks on the geiger counter as before. Then, after all the rest of the tritiated water vapour was frozen back into its container the vacuum line was pumped out as far as possible. Then with the stopcock to the pump off the upper stopcock on the geiger counter was opened. Thus the volume of tritiated water (about 1 ml.) was distributed over the total volume of the vacuum line (about 1 litre), thus reducing the actual amount of tritiated water a thousandfold. After this the upper stopcock on the geiger counter was closed, the rest of the tritiated water frozen back into its container, and the 20 ml. flask filled with counting gas. The geiger counter and 20 ml. flask is then removed to the counting apparatus as before.

During the entire filling procedure the clay sample is kept at 0°C in an ice-water mixture (or whatever the equilibration temperature was).

1. Apparatus

(i) Geiger Counter

The geiger counters used were made by Twentieth Century Electronics (Type G.A. 10M) with a stainless steel cathode and a tungsten wire anode. They were modified by the glassblower by the addition of a ground glass joint at one end (for attachment of the clay sample tube) and two vacuum stopcocks and a ground glass joint at the other end (in order to hold the tritiated water vapour prior to adding it to the geiger counter proper). The ends of the geiger counters were painted with black paint to render them insensitive to light.

(ii) Counting Apparatus

This apparatus consisted of (see Plate III)

- (a) A Phillips High Voltage Supply/Amplifier no. HW.4022.
 - (b) A Phillips Rate Meter no. P.W. 4042
 - (c) A Phillips Electronic Counter no. P.W. 4032
 - (d) A printing unit
 - (e) An electronic quench circuit (Q)
- and (f) A strip chart recorder.

The printing unit, Electronic Counter, Rate Meter and Power Supply (top to bottom) are shown in the centre of Plate III. Voltage to the geiger counter is supplied by the Power Supply through the quench unit.

2. Procedure

After the geiger counter has been filled with counting gas it is

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PLATE III

connected to the quench unit and the voltage is increased until the tube counts. This threshold voltage is usually about 1,800 - 2,000 volts and the plateau length is usually greater than 200 volts. In order to get such counting characteristics, as there is so much water vapour present in the geiger counter, it is necessary to exercise considerable care in filling the counter. The solution used for equilibration is degassed three times, and before filling the counter with counting gas the whole system (except for the actual geiger counter containing water vapour) is flushed out with the counting gas. The counting gas used is a mixture of 60% Argon and 40% Ethylene. With this gas and with the use of lead shielding it is possible to reduce the background count to about 40 counts per minute. The equivalent count in the absence of shielding is 100 - 150 counts per minute and so it can be seen that the shielding makes a significant difference to the background count. Owing to the fact that the same clay samples were used repeatedly the background in a large proportion of the experiments was more of the order of 100 counts per minute, possibly due to the fact that addition of water followed by its removal in a vacuum desiccator did not remove all the tritiated water. Also at times the vacuum line was probably slightly contaminated with traces of tritiated water from previous use.

It was necessary to examine the stopcocks on the geiger counters frequently, and at the first sign of any apparent deterioration in their coating of vacuum grease (the grease used was Apiezon "N" grease especially designed for high vacuum work) this was renewed. If this

precaution was not taken, then if even the slightest trace of air leaked into the geiger counter it became very unstable and readily went into continuous discharge. Whenever this happened the geiger counter was subsequently found to be unsatisfactory for further use unless it was first cleaned out, probably **because** when it was in continuous discharge the anode became coated with a deposit of carbon from decomposition of the ethylene gas. In an effort to restore such geiger counters to their former efficiency they were left standing in concentrated Nitric acid for some hours. They were then washed several times in distilled water and lastly in 95% Ethanol. After as much Ethanol as possible was removed the geiger counter was then connected to a vacuum pump and pumped on for a considerable time to remove the last traces of Ethanol. When this procedure proved ineffective, the geiger counters had all traces of grease and black paint (used for making the counters insensitive to light) removed and then were roasted in an oven at 550°C for some hours. They were then washed in Ethanol as before and if they were then satisfactory were repainted.

The geiger counter containing counting gas plus water vapour is operated at a voltage about 100 volts above the threshold voltage. It is allowed to operate at this voltage for some considerable time before the tritiated water is added in order to determine the background count for the particular experiment about to be performed. The pulses from the geiger counter are fed from the quench unit through the high voltage supply/amplifier to the rate meter. The rate meter is connected to

a strip chart recorder (shown on the right of Plate III) and also to an electronic counter. In most of the later experiments the pulses are also fed, after amplification, to a printing unit. This is a device by which every tenth (or hundredth etc.) count registered on the electronic counter is recorded as one unit. After a suitable interval of time (in the equipment actually used this was 15 minutes) the total number of these units is printed onto a strip of paper from where it may be read off when convenient. The advantages of the printing unit is that it averages out the count rate over a period of 15 minutes as opposed to a maximum period of 100 seconds with the rate meter. This enables a much more accurate value of the count rate to be obtained than is possible with the rate meter (and hence with the recorder) provided that the count rate is changing slowly or is stationary (even when the count rate is effectively stationary the number of counts detected in any short period of time is subject to considerable statistical fluctuation). However the printing unit is not satisfactory when the count rate is changing rapidly, as what the printing unit effectively does is to give an average value for the last 15 minutes which is taken as the actual count rate at the middle of that time interval. This will not be correct when the count rate is falling rapidly but not uniformly (as in the present work where the count rate drops very rapidly at first but eventually levels off to a steady value) as the drop in count rate over the first $7\frac{1}{2}$ minutes will be much greater than the drop over the last $7\frac{1}{2}$ minutes.

Before use (and frequently thereafter) the recorder was calibrated. (Two recorders were used in the course of the work done. The first was a 16 track Brown recorder and the second a continuous recording Kent recorder.) First the recorder was adjusted to read zero with no external connection to the rate meter. Then it was connected to the rate meter and the adjusting screws on the rate meter were adjusted so that the recorder read zero when the rate meter was reading zero, and read $\frac{30}{100}$ when the rate meter was switched to "calibrate" that is when exactly 50 cycles per second were being fed through it to the recorder. Because it was not possible to obtain a reading on the recorder with the rate meter switched to "calibrate" and actually connected to the high voltage supply/amplifier, a standardized signal was taken from the electronic counter through the high voltage supply/amplifier to the rate meter and then back to the electronic counter. It was found that the recorder connected to the rate meter showed this standardised count rate as also did the electronic counter. Thus it was shown that calibration of the recorder without the rate meter attached to the high voltage supply/amplifier is satisfactory. In order to ensure that the results given by the electronic counter (and hence the printing unit) and by the recorder were comparable, a calibration chart was prepared by counting Uranium samples at a variety of count rates over the range usually studied in the exchange experiments, and this was used to correlate the two sources of data.

After some time when the background count has been constant for a considerable period the tritiated water may be introduced. It was

occasionally found that the background count was excessively high at first (about 400 - 500 counts per minute), but this fell off to a lower (about 100 counts per minute) steady value after a short time.

At a convenient time, which is marked on the recorder chart, first the lower and then the upper stopcock on the geiger counter is opened. In this way the excess pressure in the 20 ml. flask forces the tritiated water into the geiger counter. The initial count, which was usually about 10,000 counts per minute, immediately starts to drop as the exchange of water between the clay sample and the geiger counter itself removes some of the tritiated water molecules from the sensitive volume of the geiger counter.

When the tritiated water is added it is necessary to check the plateau of the geiger counter as the threshold voltage of this may have increased due to the slight increase in pressure in the geiger counter due to opening the stopcocks through to the 20 ml. flask which was originally at a higher pressure than that of the geiger counter.

The fall off in count rate is plotted by the recorder as a function of time and in a number of the later experiments the printing unit was used after about 2 - 3 hours onwards, that is after the count rate had stopped dropping too steeply. The counting was continued out until after the count rate had reached a steady value. This was usually after about 10 - 15 hours and counting was continued until at least 20 hours. As a check that the steady value had indeed been reached, counting of one experiment was continued for 60 hours being constant from 12 hours onwards.

PROCESSING OF DATA

At the completion of each experiment the recorder chart is used to obtain the count rate at suitable intervals of time. The value given by the recorder chart is taken, a coincidence correction is added, and then the value of the background for the particular experiment is subtracted. As the half-life of Tritium (^3H) is 12.5 years,⁽¹⁴⁾ decrease in the count rate due to radioactive decay will be negligible over the duration of an experiment. The values that are obtained are then plotted on semi-logarithmic graph paper such that a graph of $\log_e(\text{count rate})$ versus time is obtained. It is found that in time the count rate falls off to a steady value "z".

The steady value "z" is now subtracted from all the points and so a new graph is obtained. It is usually found that a straight line can be drawn through the later points, that is those of lower count rate, but as one moves back towards zero time the count rate becomes higher than the straight line which intersects the zero time axis at "y". A third series of points is now obtained by subtracting the values of the line through "y" from that of the points that lie above this line. It will usually be found that a straight line can be drawn through all this series of points, cutting the zero time axis at "x". Occasionally it was found necessary to repeat the procedure and so obtain a third straight line apart from the steady value that the count rate levelled off to.

It is not necessary to allow for time taken for the tritiated water to diffuse into the geiger counter at the beginning of each

experiment. This is shown by the fact that in every experiment it is possible to neglect the first half hour and the curve will still analyse into the identical straight lines. In a number of experiments it is possible to neglect up to the first two hours without affecting the result.

MATHEMATICAL ANALYSIS OF DATA

If there are A grams of water vapour in a geiger counter of total volume V and sensitive volume v, and B grams of water adsorbed on the clay sample, then there will be an equilibrium between A and B, provided that the clay sample - water vapour system is a closed system. If the rate at which the water vapour in A is being adsorbed onto the clay sample is equal to R, then, as only the equilibrium state is being considered, the rate at which the water B is being desorbed from the clay surface will also be equal to R. Thus if the specific rate constant for the exchange is k i.e.,

9. *the plus* $R = \frac{dx}{dt} = 1$

then $R = kB$.

At zero time a suitable amount of tritiated water ($^3\text{H}^1\text{H}_2\text{O}$) is introduced into the geiger counter to give an initial count rate of about 10,000 counts/minute. The sample of tritiated water has a sufficiently high specific activity that the actual amount of water introduced into the geiger counter is not enough to upset the equilibrium between the water vapour already in the geiger counter and that adsorbed onto the clay sample. The count rate from the geiger counter falls continuously, eventually levelling off to a steady value.

Thus, if at zero time T_0 counts are introduced into the geiger counter, and at time t there are x counts in the clay sample, then there will be $(T_0 - x)$ counts remaining in the geiger counter. Thus

if the count rate is measured continuously and plotted against time on a strip chart recorder a graph of $(T_0 - x)$ versus t will be obtained. This graph will be a curve and its slope will be equal to the rate of fall of the count rate in the geiger counter, that is equal to: $\frac{dT}{dt}$

where $T = (T_0 - x) = \text{count rate at time } t$

This curve will gradually flatten out and eventually as the count rate falls to a steady value the slope will become equal to zero: that is the count rate will no longer be falling.

$\frac{dT}{dt}$ = rate at which activity is leaving the counting space +
rate at which it is entering it (as the adsorbed molecules of tritiated water are desorbed again).

$$\begin{aligned} \text{i.e. } \frac{dT}{dt} &= -\frac{R(T_0 - x)}{A} + \frac{Rx}{B} \\ &= -\frac{RT_0}{A} + \frac{Rx}{A} + \frac{Rx}{B} \end{aligned}$$

now $T = T_0 - x$

$$\therefore x = T_0 - T$$

$$\therefore \frac{dT}{dt} = -\frac{RT_0}{A} + \left(\frac{RT_0}{A} - \frac{RT}{A}\right) + \left(\frac{RT_0}{B} - \frac{RT}{B}\right)$$

$$\text{i.e. } \frac{dT}{dt} = \frac{RT_0}{B} - \left(\frac{R}{A} + \frac{R}{B}\right) T \dots \dots \dots (1)$$

In order to obtain T as a function of time it is necessary to integrate equation (1).

Can be integrated directly.

$$\text{Let } \frac{RT_0}{B} = p \text{ (a constant)}$$

$$\text{and } R\left(\frac{1}{A} + \frac{1}{B}\right) = q \text{ (a constant)}$$

then equation (1) becomes: $\frac{dT}{dt} = p - qT$

for which a particular solution is:

$$T = \frac{p}{q}$$

and thus the general solution of the differential equation (1) is:

$$T = \frac{p}{q} + u \dots \dots \dots (2)$$

where u is a function of t .

$$\therefore \frac{dT}{dt} = 0 + \frac{du}{dt}$$

and substituting in (1) one obtains:

$$\frac{du}{dt} = p - q \left(\frac{p}{q} + u \right) = -qu$$

$$\therefore \frac{du}{u} = -qdt$$

and integrating:

$$\log_e u = -qt + \text{constant}$$

and so substituting for u in (2) the most general solution is obtained:

$$T = \frac{p}{q} + ce^{-qt} \quad (c = \text{constant})$$

or substituting for p and q :

$$T = \frac{R T_0}{BR \left(\frac{1}{A} + \frac{1}{B} \right)} + ce^{-R \left(\frac{1}{A} + \frac{1}{B} \right) t}$$

$$\text{i.e. } T = \frac{T_0 A}{(A+B)} + ce^{-\frac{R(A+B)t}{AB}} \dots \dots \dots (3)$$

now when $t = 0$, $T = T_0$, and so substituting into (3)

$$T_0 = \frac{T_0 A}{(A+B)} + c$$

$$\therefore c = T_0 \left(1 - \frac{A}{(A+B)}\right) = \frac{T_0 B}{(A+B)}$$

$$\therefore T = \frac{T_0 A}{(A+B)} + \frac{T_0 B}{(A+B)} e^{-\frac{R(A+B)t}{AB}}$$

$$\text{i.e. } \frac{T}{T_0} = \frac{A}{(A+B)} + \frac{B}{(A+B)} e^{-\frac{R(A+B)t}{AB}} \dots \dots \dots (4)$$

Now when the count rate has fallen to a steady value, then this value will be the same as that for $t = \infty$, and if at $t = \infty$ $T = Z$ then from (4):

$$\frac{Z}{T_0} = \frac{A}{A+B} \dots$$

If a graph is now prepared of $\log_e T$ versus t a curve levelling off to a steady value will be obtained. This steady value may be subtracted from the rest of the curve, when the resultant graph will be a straight line. As this steady value is equal to $\frac{T_0 A}{A+B}$ the straight line will correspond to the exponential part of equation (4), and will be related to the exchangeable water "B" on the clay. For if this line cuts the $t = 0$ axis at x then as $Z \left(= \frac{A T_0}{(A+B)}\right)$ has been subtracted from the curve:

$$x = \frac{T_0 B}{A+B} \quad \text{) } \log.$$

$$\text{i.e. } \frac{x}{T_0} = \frac{B}{A+B} \dots \dots \dots (5)$$

If there are two (or more) types of exchangeable water then a total of two (or more) sloping lines will be obtained with intercepts x, y, w etc.

If the total amount of water in a geiger counter of total volume V and sensitive volume v is A grams then the amount in the sensitive volume will be $A \times \frac{v}{V}$. However, although only the fraction $\frac{v}{V}$ of the total water vapour in the geiger counter is counted, it is only necessary to compare the ratio of the count rate at two different times. Thus the quantity $\frac{v}{V}$ by which each actual count rate should be multiplied to give the true count rate corresponding to all the water in the total volume V of the geiger counter will be a common factor and so will cancel out. Thus the actual count rate T at any time t will actually be proportional to the total amount of tritiated water vapour in the geiger counter.

As was derived earlier, the rate is equal to the specific rate constant multiplied by the amount of water "B" on the clay sample.

$$\text{i.e. } R = k_p B \quad \dots \dots \dots (6)$$

The equation derived for the count rate T at any time t is:

$$\frac{T}{T_0} = \frac{A}{(A+B)} + \frac{B}{(A+B)} e^{-\frac{R(A+B)}{A B} t} \quad \dots \dots \dots (4)$$

and so the new value T^1 for the count rate after the steady value $\frac{A T_0}{A+B}$ has been removed is given by:

$$\frac{T^1}{T_0} = \frac{B}{A+B} e^{-\frac{R(A+B)}{A B} t}$$

which on substitution of the value for R from equation (6) gives:

$$\frac{T^1}{T_0} = \frac{B}{A+B} e^{-\frac{k_b (A+B)t}{A}}$$

which can be written as:

$$\log_e \left(\frac{T^1}{T_0} \cdot \frac{(A+B)}{B} \right) = - \frac{k_b (A+B)t}{A} \dots \dots \dots (7)$$

now $t_{\frac{1}{2}}$ is the time that the count rate takes to decrease to one half of its original value, and thus equation (7) reduces to:

$$\log_e \left(\frac{1}{2} \right) = - \frac{k_b (A+B)t_{\frac{1}{2}}}{A} \dots \dots \dots (8)$$

and as $-\log_e \frac{1}{2} = \log_e 2 \doteq 0.693$ equation (8) can be written as:

$$k_b = \frac{A \times 0.693}{(A+B) t_{\frac{1}{2}}} \dots \dots \dots (9)$$

If there are two (or more) types of exchangeable water ("B", "C", "D", etc.) on the clay sample, then equation (9) will apply to "B" where "B" is the type of water that exchanges fastest with the water vapour above it in the geiger counter. To obtain a similar equation for "C" the slower exchanging type of water on the clay sample, it is considered that the rate of exchange of "C" is so much slower than that of "B" that the exchange of "C" with "B" and also with "A" may be considered as indistinguishable. Thus the equation for the determination of the specific rate constant k_c for the exchange of "C" with the rest of the water present (i.e. the water in the geiger counter plus the fastest exchanging water "B" on the clay sample) will be obtained by replacing B by C and A by (A+B) in equation (9) leading to:

$$k_c = \frac{(A+B) \cdot 0.693}{(A+B+C) t_{\frac{1}{2}}} \dots \dots \dots (10)$$

where $t_{\frac{1}{2}}$ now refers to the half-time of exchange of the slower exchanging type of water "C".

If there are more types of water ("D", "E", etc.) on the clay sample, their specific rate constants (k_d , k_e , etc.) will be given by corresponding equations to equation (10) where C is replaced by D and (A+B) by (A+B+C) and so on.

If, after adding tritiated water to a sample, and replotting the data obtained on semi-logarithmic graph paper, a curve is obtained that can be resolved into a steady value (=Z) and two straight lines with intercepts with the axis $t=0$ of x and y, then the clay sample will have two types of exchangeable water on it; "B" and "C".

(A number of those graphs, resolved into straight lines, will be found in the section containing experimental data page 43).

When the count rate, as measured in the geiger counter, has fallen to a steady value, the tritiated water will be distributed in equilibrium between the geiger counter and the clay sample. If it is assumed that tritiated water ($^3\text{H } ^1\text{H}_2\text{O}$) distributes itself in the same ratio as ordinary water (H_2O), then the ratio of the radioactivity will be the same as the ratio of the bulk of water present. As the final count rate (steady value) is equal to the initial count rate minus the amount of tritiated water adsorbed onto the clay the ratios:

$$\frac{\text{final count (steady value)}}{\text{initial count}}$$

and $\frac{\text{water vapour in counter}}{\text{water vapour in counter} + \text{water adsorbed onto clay}}$

will be equal. That is, for two types of water on the clay "B" and "C"

$$\frac{Z}{T_0} = \frac{A}{A+B+C} \dots \dots \dots (11)$$

When considering only one exchangeable type of water the relationship:

$$\frac{x}{T_0} = \frac{B}{A+B} \dots \dots \dots (5)$$

was obtained, and in the case of two (or more) types of exchangeable water this equation will still be valid for the fastest exchanging type of water, as it is obtained from the exponential term for the fastest exchanging type of water (if there is more than one type) by putting $t = 0$ in the equation obtained by removing the steady value and also the exponential terms for any slower exchanging types of water.

If the second line corresponding to the water "C" cuts the $t = 0$ axis at y , then y will be related to the amount of activity and hence to the total amount of exchangeable water "C". However all the activity apart from that in "C" is "A" and "B" (assuming that the rate of exchange of "C" with "A" is much less than that of "B" with "A") and only the fraction of this activity in "A" will be counted. Therefore to obtain the amount of water in C it will be necessary to multiply y by the ratio $\frac{A+B}{A}$. Then if B is replaced by C and A by (A+B) as in the derivation of equation (10), the equation:

$$\frac{y}{T_0} \times \frac{(A+B)}{A} = \frac{C}{A+B+C} \dots \dots \dots (12)$$

is obtained. Similar reasoning leads to the equation:

$$\frac{W}{T_0} \times \frac{(A+B+C)}{A} = \frac{D}{A+B+C+D} \dots \dots \dots (13)$$

where W is the intercept of the line, corresponding to a third, even more slowly exchanging type of water, with the $t = 0$ axis.

As "A" may be obtained from a knowledge of the volume of the geiger counter and the relative humidity and temperature at which the experiment is being performed, "B" may be calculated from equation (5). T_0 is equal to $Z + x + y + w + \dots$ that is to the steady value plus the value of each line where it cuts the $t = 0$ axis. Once "B" is known "C" may then be calculated from equation (12). If there are any other types of water the amounts of each may be calculated in turn by the use of equation (13) etc.

As a check the total amount of adsorbed water on the clay may be calculated from equation (11) and this should be equal to the sum of "B", "C", "D" etc., as calculated individually. It can be shown mathematically that equation (11) can be derived from equations (5) and (12) and is not independent of them.

EXPERIMENTAL

Five samples of Montmorillonite containing the exchangeable cations Potassium, Hydrogen, Lithium, Barium and Magnesium were prepared and studied. Potassium Montmorillonite was studied over a range of relative humidities from 1.66% to 96% (all at 0°C) and from the data obtained a phase diagram was prepared. (Figure 2). Hydrogen Montmorillonite was also studied over a similar range of relative humidities at 0°C and a phase diagram prepared. (Figure 3). Experiments were performed at two other temperatures (-21.3°C and 25.0°C) on Hydrogen Montmorillonite in order to determine the activation energies of the different types of water detected. For Barium and Lithium Montmorillonites experiments were performed at 18.7% and 78% relative humidity, and Magnesium Montmorillonite was examined at 78% relative humidity. Also two different forms of Allophane of different ages, Allophane "B" and Allophane "A" were examined at 78% relative humidity.

I Potassium Montmorillonite

Experiments were carried out on Montmorillonite saturated with Potassium ions at relative humidities ranging from 1.66% to 96% and at 0°C. At 96% relative humidity it was found that the log (count rate) versus time graph could be resolved into four straight lines corresponding to the steady value plus three different types of water. All other experiments at relative humidities at up to 88.5% were analysed into three straight lines corresponding to two different types of water. In each experiment the amounts of each type of water and also its specific rate constant were calculated and are given in table I.

Figure 2

Figure 3

Graph of
Basal Spacing versus Relative Humidity
(see Brindley¹⁸)

see p. 70

TABLE I

Relative Humidity (%)	Amount of water "B" gms/gm clay $\times 10^2$	Amount of water "C" gms/gm clay $\times 10^2$	Amount of water "D" gms/gm clay $\times 10^2$	Specific rate constants hours ⁻¹		
				k_b	k_c	k_d
1.66	0.0107	0.0537	-	0.735	0.111	-
18.7	0.165	0.813	-	1.11	0.192	-
45.4	0.538	2.98	-	0.796	0.205	-
78.0	0.923	6.77	-	1.04	0.158	-
88.5	2.77	8.55	-	0.928	0.177	-
96.0	1.49	2.78	38.95	0.958	0.546	0.0495

It will be seen that the amount of water "B" at 88.5% relative humidity is considerably greater than might be expected from the amounts of this type of water at 78% and 96% relative humidity. In some experiments where two types of water were expected only one type was observed. It is believed that the reason for this is that both types of water are undergoing exchange with the same half-time. If there are actually two types of water then the expressions for the two specific rate constants k_b and k_c are: (see Mathematical Analysis of Data p. 31).

$$k_b = \frac{A}{A+B} \times \frac{0.693}{t_{\frac{1}{2}}^b} \dots \dots \dots (1)$$

$$\text{and } k_c = \frac{A+B}{A+B+C} \times \frac{0.693}{t_{\frac{1}{2}}^c} \dots \dots \dots (2)$$

and if $t_{\frac{1}{2}}^b = t_{\frac{1}{2}}^c$ then division of (1) by (2) gives:

$$\frac{k_b}{k_c} = \frac{A(A+B+C)}{(A+B)^2} \dots \dots \dots (3)$$

Now if k_b and k_c are known from other experiments, then the left hand side of equation (3) can be calculated. Also, if the total amount of water on the clay (which is apparently of only one type) = B^1 , and from experiments at the same relative humidity but with different amounts of clay the ratio C/B is known, then the quantity B^1 can be split up into two types of water in the same ratio as C/B . If these new values are substituted into the right-hand side of equation (3) then the ratio $\frac{A(A+B+C)}{(A+B)^2}$ can be calculated. In the experiments where this phenomenon was observed it was found that the right-hand side and the left hand side of equation (3) were at least approximately equal.

Because of this it was thought that the quantity "B" observed in the experiment at 88.5% relative humidity might actually be composed of two different types of water. From a comparison with experiments on Hydrogen Montmorillonite, where only two types of water were observed at all relative humidities up to 96%, with the water "C" increasing very greatly between 88.5% and 96% relative humidity, it seems that in the experiment on Potassium Montmorillonite at 96% relative humidity the type of water "D" actually corresponds to the type "C" observed at lower relative humidities. From a consideration of a graph of "B" versus relative humidity the amount of "B" expected

at 88.5% relative humidity would be about 1.14×10^{-3} grams of water.

(It is necessary to use the actual amounts of water, not grams of water/gram of clay in equation (3)). As the total amount of "B" at 88.5% relative humidity is 2.52×10^{-3} grams of water it would appear that there is $(2.52 - 1.14) \times 10^{-3} = 1.38 \times 10^{-3}$ grams of water of a third type. This amount is less than that observed for type "C" at 96% relative humidity, and so would be expected to be the same type of water as this. The specific rate constant k_c may be taken to be that obtained from the data at 96% relative humidity, while k_b will be the average value of this quantity over all relative humidities ($= 0.928 \text{ hours}^{-1}$). Thus the ratio k_b/k_c is $\frac{0.928}{0.546} = 1.70$. It is also found that, using the value of "B" at 88.5% relative humidity as calculated above by extrapolation, the ratio $\frac{A(A+B+C)}{(A+B)^2} = 1.71$ which is in good agreement with the value expected from the ratio k_b/k_c i.e. 1.70.

From the above calculations it appears that there are three types of water on Potassium Montmorillonite at 88.5% relative humidity. If it is assumed that the increase in this third type is linear with increasing relative humidity (as is found to be approximately the case with the first type "B") then extrapolation shows that there is none of this third type below about 80% relative humidity, and that the amount increases to 3.2×10^{-2} grams of water/gram of clay at 100% relative humidity. It would be possible to determine with more certainty whether or not the third type of water does increase linearly with increasing relative humidity by doing experiments at other relative

humidities between 80% and 100%.

II Hydrogen Montmorillonite

The samples of Hydrogen Montmorillonite were prepared as described earlier (Preparation of clay samples p. 9). By using the ion-exchange resin it is possible to remove all other ions such as Aluminium from the clay. However whenever pure Hydrogen Montmorillonite is prepared it is not stable, and Aluminium is slowly liberated. At first the amount of Aluminium present will be small and will exist as Al^{+3} ions each of which would be expected to have six water molecules around them. However their number will be so small that the amount of water thus associated would be very little and so would not be detected by the technique being used. As the amount of Aluminium increases complex cations are formed between Aluminium ions by the elimination of water. Thus the actual amount of water associated with the Aluminium ions stays very small as the liberation of Aluminium proceeds. Bolt and Warkentin (15) have studied the rate at which Aluminium is liberated from pure Hydrogen Montmorillonite (prepared in a similar manner to the procedure used here), and they found that after 10 days there was still a considerable fraction of Hydrogen ions present. Their studies were made on clay samples in continuous contact with water, whereas in the present work the only time in which there was excess water in contact with the clay sample was after each experiment when the samples were wetted with 1-2 ml. water and then dried in a vacuum dessicator to remove the radioactivity present on the clay. It might be expected that the process of liberation of the Aluminium ions would be much more rapid when the clay was in contact with water than when it was dry. Thus it

seems probable that the majority at least, of experiments would be performed on samples that had predominantly Hydrogen ions as their replaceable cations. One sample was used for the ^{most} majority of the work and some nine months after it was first prepared it was found that water in equilibrium with it had a pH of 3.2 (± 0.1).

Experiments were performed at a number of relative humidities from 0.31% up to 96% at 0°C. In all cases it was found that there were only two types of water present on the clay. The changes in the amounts of the two different types of water with changing relative humidity are shown in Figure 3.

Experiments were also performed at -21.3°C and 45.4% relative humidity and at +25.0°C and 11.5% relative humidity, and from the values calculated for k_b and k_c at these temperatures, as well as at 0°C, the activation energies for the two different types of water "B" and "C" were determined.

III Montmorillonites containing other Exchangeable Cations

Samples of Montmorillonite saturated with Lithium, Barium and Magnesium ions were studied at 78% relative humidities and in each case only two types of water were detected. The Lithium and Barium clays were also studied at 18.7% relative humidity. It was found that there were only two types of water present on the Barium clay, but there appeared to be three different types of water on the Lithium clay at this relative humidity. It seems very unlikely that there would be fewer types of water at high than at low relative humidities. Study of the amounts of water "B" on the various clay samples at 78% relative

humidity (Table II) shows that the amount of this type of water present on the Lithium clay is excessively large.

TABLE II

(relative humidity = 78%)

Exchangeable cation	Amount of water "B" gms/gm clay ($\times 10^2$)	Amount of water "C" gms/gm clay ($\times 10^2$)
H ⁺	0.78	9.63
Li ⁺	4.45	9.01
Ba ⁺	0.74	7.74
Mg ⁺	1.59	7.03
K ⁺	0.92	6.77

Also by considering the ratio $\frac{\text{"C"}}{\text{"B"}}$ for Lithium clay at 78% relative humidity and the ratio $\frac{\text{"C"}}{\text{"B" + "D"}}$ at 18.7% relative humidity it will be seen that they are quite similar (all values in gms water/gm. clay $\times 10^2$).

$$\frac{C}{B} \text{ (78\% R.H.)} = \frac{9.01}{4.45} = 2.03$$

$$\text{and } \frac{C}{B+D} \text{ (18.7\% R.H.)} = \frac{4.54}{0.54 + 1.61} = 2.11$$

Thus it seems likely that there are actually three different types of water present on lithium clay at 78% relative humidity, two of which are appearing as the same type.

IV Allophanes

Two samples of Allophane were analysed at 78% relative humidity. In both samples two different types of water were observed. Also the

specific rate constants (k_b) for the first type of water were similar. However the specific rate constants for the second type of water are quite different (Table III). This difference may mean that the two clays have different second types of water, or else that the experimental results are not sufficiently reliable in this case. The latter conclusion is quite possible because the experiments were performed once only and should be checked before any definite conclusion is drawn.

TABLE III

	k_b	k_c
Allophane "B"	0.0661 hours ⁻¹	0.318 hours ⁻¹
Allophane "A"	0.0714 hours ⁻¹	0.110 hours ⁻¹

From Table III it can be seen that the specific rate constant k_c is, for both samples of clay, greater than k_b . Thus it seems that, in the case of Allophane, the first type of water is bound more tightly to the clay than the second type.

Results for the various experiments which have been described are represented in graphical form in the following pages. Where more than one experiment has been performed at a particular relative humidity only one typical graph of the results is shown. In the graphs the amount of water vapour in the geiger counter is designated as "A". It is calculated from the relative humidity and the volume of the geiger counter. The amounts of the different types of water adsorbed onto the clay (as calculated from the intercepts x , y , w , z and "A") are designated as "B", "C" and "D" (if there are three types), and the specific rate constants for these types of water as k_b , k_c and k_d . The water designated as "B" has the highest specific rate constant (k_b) (and thus exchanges at the fastest rate), the water "C" has the next highest specific rate constant (k_c) and so on.

No.
highest
rate

The temperature, relative humidity, and weight of the clay sample used are also recorded on each graph.

The graphs are arranged as follows:

- (1) Potassium Montmorillonite pages 44 - 49
- (2) Hydrogen Montmorillonite pages 50 - 56
- (3) Lithium, Barium and Magnesium Montmorillonite pages 57 - 61
- (4) Allophanes pages 62 - 63

POTASSIUM MONTMORILLONITE

Relative Humidity = 1.66%

Temperature = 0°C

Wt. of clay = 0.091 gm.

Wt. of "A" = 0.891×10^{-5} gm.Wt. of "B" = 0.97×10^{-5} gm.Wt. of "C" = 4.89×10^{-5} gm. $k_b = 0.735 \text{ hours}^{-1}$ $k_c = 0.111 \text{ hours}^{-1}$

POTASSIUM MONTMORILLONITE

Relative Humidity = 18.7%

Temperature = 0°C

Wt. of clay = 0.091 gm.

Wt. of "A" = 0.101×10^{-3} gm.Wt. of "B" = 0.15×10^{-3} gm.Wt. of "C" = 0.74×10^{-3} gm.

$$k_b = 1.11 \text{ hours}^{-1}$$

$$k_c = 0.192 \text{ hours}^{-1}$$

COUNT RATE (c.p.m.)

POTASSIUM MONTMORILLONITE

Relative Humidity = 45.4%

Temperature = 0°C

Wt. of clay = 0.091 gm.

Wt. of "A" = 0.244×10^{-3} gm.Wt. of "B" = 0.49×10^{-3} gm.Wt. of "C" = 2.71×10^{-3} gm.

$$k_b = 0.796 \text{ hours}^{-1}$$

$$k_c = 0.205 \text{ hours}^{-1}$$

POTASSIUM MONTMORILLONITE

Relative Humidity = 78%

Temperature = 0°C

Wt. of clay = 0.091 gm.

Wt. of "A" = 0.419×10^{-3} gm.Wt. of "B" = 0.84×10^{-3} gm.Wt. of "C" = 6.16×10^{-3} gm.

$$k_b = 1.04 \text{ hours}^{-1}$$

$$k_c = 0.158 \text{ hours}^{-1}$$

POTASSIUM MONTMORILLONITE

Relative Humidity = 88.5%

Temperature = 0°C

Wt. of clay = 0.091 gm.

Wt. of "A" = 0.475×10^{-3} gm.Wt. of "B" = 2.52×10^{-3} gm.Wt. of "C" = 7.80×10^{-3} gm. $k_b = 0.928 \text{ hours}^{-1}$ $k_c = 0.177 \text{ hours}^{-1}$

POTASSIUM MONTMORILLONITE

Relative Humidity = 96 %

Temperature = 0°C

Wt. of clay = 0.091 gm.

Wt. of "A" = 0.515×10^{-3} gm.Wt. of "B" = 1.35×10^{-3} gm.Wt. of "C" = 2.52×10^{-3} gm.Wt. of "D" = 35.41×10^{-3} gm.

$$k_b = 0.958 \text{ hours}^{-1}$$

$$k_c = 0.546 \text{ hours}^{-1}$$

$$k_d = 0.0495 \text{ hours}^{-1}$$

HYDROGEN MONTMORILLONITE

50

Relative Humidity = 18.7%

Temperature = 0°C

Wt. of clay = 0.056 gm.

Wt. of "A" = 0.101×10^{-3} gm.

Wt. of "B" = 0.12×10^{-3} gm.

Wt. of "C" = 2.24×10^{-3} gm.

$k_b = 1.55 \text{ hours}^{-1}$

$k_c = 0.052 \text{ hours}^{-1}$

HYDROGEN MONTMORILLONITE

Relative Humidity = 45.4%

Temperature = 0°C

Wt. of clay = 0.056 gm.

Wt. of "A" = 0.244×10^{-3} gm.Wt. of "B" = 0.19×10^{-3} gm.Wt. of "C" = 4.54×10^{-3} gm.

$$k_b = 2.59 \text{ hours}^{-1}$$

$$k_c = 0.067 \text{ hours}^{-1}$$

HYDROGEN MONTMORILLONITE

Relative Humidity = 78%

Temperature = 0°C

Wt. of clay = 0.056 gm.

Wt. of "A" = 0.419×10^{-3} gm.Wt. of "B" = 0.44×10^{-3} gm.Wt. of "C" = 5.39×10^{-3} gm. $k_b = 1.69 \text{ hours}^{-1}$ $k_c = 0.107 \text{ hours}^{-1}$

HYDROGEN MONTMORILLONITE

Relative Humidity = 88.5%

Temperature = 0°C

Wt. of clay = 0.056 gm.

Wt. of "A" = 0.475×10^{-3} gm.Wt. of "B" = 0.51×10^{-3} gm.Wt. of "C" = 6.02×10^{-3} gm. $k_b = 1.02 \text{ hours}^{-1}$ $k_c = 0.097 \text{ hours}^{-1}$

HYDROGEN MONTMORILLONITE

Relative Humidity = 96%

Temperature = 0°C

Wt. of clay = 0.056 gm.

Wt. of "A" = 0.515×10^{-3} gm.Wt. of "B" = 0.55×10^{-3} gm.Wt. of "C" = 19.50×10^{-3} gm.

$$k_b = 1.65 \text{ hours}^{-1}$$

$$k_c = 0.052 \text{ hours}^{-1}$$

HYDROGEN MONTMORILLONITE

Relative Humidity = 45.4%

Temperature = -21.3°C

Wt. of clay = 0.056 gm.

Wt. of "A" = 0.0365×10^{-3} gm.Wt. of "B" = 0.10×10^{-3} gm.Wt. of "C" = 1.29×10^{-3} gm. $k_b = 0.344 \text{ hours}^{-1}$ $k_c = 0.016 \text{ hours}^{-1}$

HYDROGEN MONTMORILLONITE

Relative Humidity = 11.5%

Temperature = +25.0°C

Wt. of clay = 0.040 gm.

Wt. of "A" = 0.319×10^{-3} gm.Wt. of "B" = 0.33×10^{-3} gm.Wt. of "C" = 2.14×10^{-3} gm.

$$k_b = 1.48 \text{ hours}^{-1}$$

$$k_c = 0.313 \text{ hours}^{-1}$$

COUNT RATE (c.p.m.)

LITHIUM MONTMORILLONITE

Relative Humidity = 78%

Temperature = 0°C

Wt. of clay = 0.025 gm.

Wt. of "A" = 0.419×10^{-3} gm.Wt. of "B" = 1.05×10^{-3} gm.Wt. of "C" = 2.60×10^{-3} gm. $k_b = 0.581 \text{ hours}^{-1}$ $k_c = 0.380 \text{ hours}^{-1}$

BARIUM MONTMORILLONITE

Relative Humidity = 18.7%

Temperature = 0°C

Wt. of clay = 0.025 gm.

Wt. of "A" = 0.101×10^{-3} gm.Wt. of "B" = 0.055×10^{-3} gm.Wt. of "C" = 0.802×10^{-3} gm. $k_b = 1.50 \text{ hours}^{-1}$ $k_c = 0.102 \text{ hours}^{-1}$

BARIUM MONTMORILLONITE

Relative Humidity = 78%

Temperature = 0°C

Wt. of clay = 0.080 gm.

Wt. of "A" = 0.419×10^{-3} gm.Wt. of "B" = 0.71×10^{-3} gm.Wt. of "C" = 6.20×10^{-3} gm.

$$k_b = 0.852 \text{ hours}^{-1}$$

$$k_c = 0.0845 \text{ hours}^{-1}$$

MAGNESIUM MONTMORILLONITE

Relative Humidity = 78%

Temperature = 0°C

Wt. of clay = 0.085 gm.

Wt. of "A" = 0.419×10^{-3} gm.Wt. of "B" = 1.33×10^{-3} gm.Wt. of "C" = 5.84×10^{-3} gm. $k_b = 0.417 \text{ hours}^{-1}$ $k_c = 0.159 \text{ hours}^{-1}$

ALLOPHANE "A"

Relative Humidity = 78%

Temperature = 0°C

Wt. of clay = 0.110 gm.

Wt. of "A" = 0.419×10^{-3} gm.Wt. of "B" = 5.99×10^{-3} gm.Wt. of "C" = 15.46×10^{-3} gm. $k_b = 0.0714 \text{ hours}^{-1}$ $k_c = 0.110 \text{ hours}^{-1}$

A. Potassium and Hydrogen Montmorillonite Phase Diagrams

In both Hydrogen and Potassium Montmorillonites over a wide range of relative humidities two different types of water were observed. Also in the case of Potassium Montmorillonite a third type of water is present from about 80% relative humidity onwards. Comparison of the phase diagrams (Figures 2 and 3) will show that, apart from the fact that there is considerably more of the type of water "C" at low relative humidities in the case of Hydrogen Montmorillonite and the appearance of the third type of water in the Potassium Montmorillonite phase diagram, the two diagrams are essentially similar. Thus it can justifiably be said that the two types of water "B" and "C" are the same in both cases.

(1) Water of hydration of exchangeable cations

One possible explanation of one of these two types of water is that it is water associated with the exchangeable cations (i.e. Hydrogen or Potassium) on the clay. This would be in agreement with the work of Ganguly and Gupta ⁽¹⁰⁾ who state that the exchangeable cations including Hydrogen of oven-dry clay minerals are present in the hydrated form. However the amounts of both types of water increase continuously from very low ($\sim 1\%$) relative humidities upwards whereas if the above theory was true it would be expected that there would be one type of water present in an almost constant amount from about zero relative humidity upwards.

A consideration of the amounts of each type of water present

suggests that neither is associated with the exchangeable cations. The amount of the water "B" is always relatively small. Even at 80% relative humidity the amount of "B" present is only about 0.010 gms. water/gm. of clay for Potassium Montmorillonite (and even less for Hydrogen Montmorillonite), and the amount needed to have even one water molecule per Potassium ion is 0.017 gms. water/gm. clay. The type of water "C" on the other hand, while being of a more suitable amount for cation hydration at lower relative humidities increases rapidly above about 90% relative humidity to a value far too large to be associated with the cations.

The third type of water on Potassium Montmorillonite is believed to be associated with the Potassium ions present in the clay. It seems reasonable that while water may be associated with the Potassium ions and so give a third type of water, the Hydrogen ions in Hydrogen Montmorillonite may be small enough to be buried so far down into the clay structure that there is not enough room for any water molecules to group themselves around them. If, however, there were water molecules associated with the Hydrogen ions these might not differ so much from ordinary water molecules as might those associated with the Potassium ions. Thus any such water in the Hydrogen clay might not be distinguishable from ordinary water molecules (say water of type "C") associated with the clay surfaces, and so would not appear as a new type of water but would be incorporated into "C". If there are actually two indistinguishable types of water incorporated into "C" at high ($\sim 96\%$) relative humidities it might be possible to distinguish between them, if they have different

activation energies, by studying Hydrogen Montmorillonite at different temperatures to 0°C and at 96% relative humidity. It may be found that at some other temperature there are three different types of water on the clay at this relative humidity. Also, if there was water associated with the Hydrogen ions present, the amount would diminish as the Aluminium from a breakdown of the clay structure replaced the Hydrogen ions, and so there would be less of this water than in the case of any other ion.

As stated earlier, extrapolation of this third type of water to 100% relative humidity gives a value for the amount expected at this relative humidity of 3.2×10^{-2} gms. water/gram of clay. As the amount of water required for one molecule of water per Potassium ion is 0.017 gms./gm. of clay, it appears that, providing the extrapolation is justifiable, there are $\frac{0.032}{0.017} \approx 1.9$ molecules of water/Potassium ion at 100% relative humidity. Robinson and Stokes⁽¹⁶⁾ have obtained hydration numbers for whole molecules by activity coefficient data. They obtain the values:

<u>Salt</u>	<u>n (= hydration number)</u>
KCl	1.9
KBr	2.1
KI	2.5

From data obtained from studies of these and other salts they conclude that the anions are very little hydrated if at all, but that they increase in hydration with increasing size. From the calculations above it seems that there are 1.9 water molecules/Potassium ion, and if this is so it would seem that the Chloride ion is not hydrated at

all, which is quite a reasonable conclusion. A necessary assumption is that, at least at 100% relative humidity, the Potassium ions be sufficiently detached from the surface of the clay to permit this amount of hydration around them. As the average number of surrounding water molecules is only 1.9/Potassium ion it would be possible for the ion to still be attached to at least one point on the clay surface. However, for Lithium or one of the Alkaline Earth ions, which apparently have a considerably greater number of water molecules around them⁽¹⁶⁾, this attachment would not be possible. Thus it would be of considerable interest to prepare a phase diagram for one of these ions. If this assumption can be justified this technique of extrapolating the phase diagram could be used to determine the hydration numbers of single ions.

Robinson and Stokes⁽¹⁷⁾ have obtained individual hydration numbers for single ions from diffusion measurements. They have obtained two alternative sets of values depending on whether the value for the Ammonium ion is $n = 0.0$ or $n = 0.5$. (All the ionic hydration numbers from diffusion are considerably lower than those obtained from activity coefficient studies because they are multiplied by an undetermined factor less than unity. See Robinson and Stokes⁽¹⁷⁾.) Preparation of a phase diagram for Montmorillonite saturated with Ammonium ions would enable the amount of water, if any, attached to the Ammonium ions at 100% relative humidity to be determined, and it would be possible to distinguish between no water molecules around the Ammonium ion (when there would be no third type of water detected) and a positive value (≥ 0.5 water molecules/ammonium ion) for this quantity.

The present results suggest that Potassium ions only become hydrated at high ($\sim 80\%$) relative humidities. They differ from the work of Hendricks, Nelson and Alexander⁽¹⁾ who found, from Differential Thermal Analysis studies, that those ions that are hydrated, are hydrated at very low ($\sim 5-10\%$) relative humidities. From their analysis of the Differential Thermal Analysis curves they came to the conclusion that the Potassium ion of Potassium Montmorillonite was not hydrated at all. However as they made no attempt to resolve the Differential Thermal Analysis peaks for above 70% relative humidity they would not have determined the presence of water of hydration of the Potassium ions at above 80% relative humidity anyway.

(2) Other types of water present

If the third type of water apparent in the phase diagram of Potassium Montmorillonite is associated with the Potassium ions present then the other two types must be associated with the clay surface in some way.

Hendricks et. al.⁽¹⁾ came to the conclusion that there were two different types of water on Montmorillonite (apart from cationic water), namely an unimolecular layer of water molecules attached to the clay surface, and a second layer of water molecules attached to the surface of the first layer. If this was so, then as Montmorillonite consists of repeating Silicate-Aluminate-Silicate layers, the second layer of water would, as well as being bound to the water molecules of the first layer on one side, be bound to the Silicate layer of the next unit cell. Thus in effect the situation would be as shown in Figure 4:

Figure 4

and where there were two unimolecular water layers one on top of the other (as in the middle of figure 4) both layers would be the same from the point of view of ~~radioactive~~ exchange with tritiated water molecules. If, however, there is less of the second layer than of the first layer, then there will be sections of the clay where, because of the proximity of a double layer of water molecules, the opposite surfaces of the clay are far enough apart to accommodate two layers, but there is only one layer of water molecules. In this case the single layer of water molecules will only be bonded on one side and so might be expected to have a different specific rate constant, probably being bonded less strongly. It is believed that at most relative humidities Montmorillonite is a mixture of single and double layers of water molecules. If there is only a single layer of water molecules between the silicate sheets then it will be bound on both sides and so would be expected to be similar to double layers of water as far as ^{water}/exchange reactions are concerned. This suggests a possible explanation for the two different types of water observed on the clay. The type of water "B" which is present in much smaller

amounts than "C" also has the fastest rate of exchange. This would be expected from the above theory as the amount of water that is not bound on one side (inbetween sheets where there are two or more layers in at least some areas) would not be nearly as large as the amount of either single layers or multilayers of water.

Thus it appears that the larger amount of water "C" is equal to the bulk of the water between the silicate layers. Confirmatory evidence for this hypothesis comes from X-ray diffraction studies. The work of Nagelschmidt ⁽⁸⁾ and of Hofmann and Bilke ⁽⁹⁾ whose results have been correlated by Brindley ⁽¹⁸⁾ (see p. 35C) shows that the basal spacing of Montmorillonite as a function of relative humidity follows a similar pattern to the phase diagrams prepared in the present work. The graph of basal spacing versus relative humidity increases rapidly at first from a spacing of about $10.5 - 11 \text{ \AA}$ to about $14 \text{ \AA}$ at about 15% relative humidity, and then the spacing is of the order of about $14-15 \text{ \AA}$ until a relative humidity of about 80% is reached, after which the spacing increases rapidly to a value of about $20 \text{ \AA}$ at 100% relative humidity. As the expected basal spacing for dry Montmorillonite would be about $10.0 - 10.5 \text{ \AA}$ with an increase of $2.5 - 3.0 \text{ \AA}$ for each layer of water molecules it will be seen that at moderate values of relative humidity (20 - 80%) there is at least some Montmorillonite containing two layers of water molecules, while at very high relative humidities the spacing increases to a value ($20 \text{ \AA}$) comparable to that expected for four layers of water. This behaviour is just what is expected

from the phase diagrams (Figures 2 and 3, pages 35a and 35b), the amounts of water observed at 96% relative humidity (approximately 0.4 grams of water/gram of clay) for "C" being equivalent to four layers of water, as it has been calculated that the amount of water required for one unimolecular layer of water molecules is 0.10 grams of water/gram of clay.

From a study of the Montmorillonite basal spacing versus relative humidity graph as given by Brindley ⁽¹⁸⁾ (see page 35c) it can be seen that the actual spacing at low relative humidities is less for the Sodium clay than for the Hydrogen clay. This would suggest that there is more water between the silicate sheets at low relative humidities in the Hydrogen clay, and this is in accordance with the results obtained in the present work, the amount of "C" for the Hydrogen clay being greater than the amount for the Potassium clay. A possible explanation for this is that in the Hydrogen clay the presence of even a few Aluminium ions will hold the adjoining silicate layers further apart than other cations especially Potassium which is of a suitable size to fit into the "holes" in the surface of the clay.

Another possible explanation of the existence of two different types of water on Montmorillonite, apart from water of hydration of the exchangeable cations present, is that one type is water actually on the outer surface of the clay particles. If this were so, and the outer surface water were type "B", then as this would be bounded by the clay surface on one side only, it would be expected to exchange more rapidly than internal water. This is true in as far as "B" has a higher specific rate constant than the water "C". Such a hypothesis

would necessitate "C" being all the water adsorbed onto the clay surface except the outside surfaces. This would still be in accordance with the X-ray diffraction data already described. The amount of "B" which is of the order of 0.01 gms. water/gm. clay, while only enough for about $\frac{1}{10}$ of an unimolecular layer over all the interlamellar surfaces, would be enough for several layers on the outside of the clay particles. Hendricks et. al.⁽¹⁾ have calculated, from a comparison of total water adsorption and gas (N₂, O₂) adsorption onto Montmorillonite that the Montmorillonite particles that they studied (<2 μ equivalent spherical diameter - the same size range as was used in the present work) contain about 50 - 100 Silicate layers. This value is within the range indicated by electron diffraction and interference of visible light. Thus the amount of "B" present would be enough for 5-10 layers of water molecules on the outside of the clay. Such a situation is not supported by the interpretation of the activation energy studies as given in the following section.

B. Activation Energy Studies on Hydrogen Montmorillonite

As the reactions being studied (that is the exchange of water molecules in the vapour and adsorbed states) is a first order reaction it is possible to apply the Arrhenius activation energy formula viz:

$$\log_e k = \text{const.} - \frac{E}{RT}$$

where E = energy of activation

R = gas constant

T = absolute temperature

k = specific rate constant

Thus it is possible for the energy of activation to be calculated from a knowledge of the rate constants at different temperatures. In the present work rate constants (k_b and k_c) are calculated for both types of water on Hydrogen Montmorillonite at 298.0°A ($+25^\circ \text{C}$); 273.0°A (0°C) and 251.7°A (-21.3°C) and a graph of $\log_e k$ versus $\frac{1}{T}$ is prepared (Figure 5.)

The energy of activation E_c for the slower exchanging type of water "C" is calculated from the line "c" to be 9,800 calories. On examination of the rate constant data for the faster exchanging type of water "B" it is found that between -21.3°C and 0°C the specific rate constant k_b increases with increasing temperature, but has almost the same value at $+25.0^\circ \text{C}$ as at 0°C . Consequently the activation energy is very low for the water "B" in this range. This suggests that the water "B" is very loosely bound to the clay surface above 0°C , and so exchanges very readily with the water vapour above it in the equilibrium system being studied.

From the experiments performed it is not possible to tell exactly at what temperature the activation energy of the water "B" increases from the very low value it apparently has between 0°C and $+25^\circ \text{C}$. It is conceivable that the specific rate constant k_b has a very similar value until some temperature slightly below 0°C before starting to decrease with temperature until it has the value observed at -21.3°C . The exact temperature at which the specific rate constant starts to change could be calculated by performing another experiment between 0°C and -21.3°C , say at -10°C . The required temperature

Graph of
 $\text{Log}_e k_b (\bullet \text{---})$ vs. $1/T$
 and $\text{Log}_e k'_c (* \text{---})$ vs. $1/T$
 for Hydrogen Montmorillonite

Figure 5

would then be given by the intersection of the lines between $+25.0^{\circ}\text{C}$ and 0°C and between -10°C and -21.3°C .

In order to seek a likely explanation for the change in activation energy at (or possibly slightly below) 0°C it is necessary to consider the way in which the water molecules may be arranged on the clay surface. The surface of Montmorillonite consists of hexagonal rings of oxygen atoms. A number of ways in which water molecules may be adsorbed onto this surface have been suggested. One of the most satisfactory arrangements is that given by Hendricks et. al. in their paper on the hydration mechanisms of Montmorillonite ⁽¹⁾, which is depicted below:

Figure 6

In the above figure the Oxygen atoms in the water molecules are shown as large circles and the Hydrogen atoms shown as small circles. The full lines (—————) represent O - H bonds and the dashed lines (- - - - -) represent Hydrogen bonds. The clay surface consists of hexagonal rings of Oxygen atoms which are directly underneath the Oxygen atoms of the water molecules shown in Figure 6. It will be seen that every second water molecule has one of its Hydrogen atoms pointing downward (represented as a small circle inside the large circle of the Oxygen atom), and Hydrogen bonded to one of the Oxygen atoms of the clay surface.

The advantage of an arrangement such as is described above is that it propagates the lattice of Oxygen atoms as a whole. Also it will be seen that those water molecules that do not have a Hydrogen atom Hydrogen bonded to the clay surface are Hydrogen bonded in three places (once to the Oxygen atom and once to each Hydrogen atom) whereas the other water molecules are Hydrogen bonded in four places (twice to the Oxygen atom and once to each Hydrogen atom). Thus it would be possible to have another water molecule Hydrogen bonded through one of its Hydrogen atoms to the water molecule in the first layer with only three Hydrogen bonds. In this way it would be possible to have a second layer of water molecules on top of the first layer with exactly the same arrangement as the first layer but rotated through 60° . Where there was a second layer of water molecules on top of the first layer, the individual water molecules of the second layer would also be Hydrogen bonded in either three or four places, and so would be expected to have

approximately the same activation energy as the first layer. If there was another hexagon of Oxygen atoms present adjacent to the upper surface of the top layer of water molecules, then it would be expected that the sheet of water molecules could link itself to this hexagon in a similar manner to the way in which the water molecules were attached to the lower surface of the clay on which they are considered to have condensed. Thus all the water molecules would be Hydrogen bonded in four ways.

On the basis of this adsorption model it is possible to suggest an explanation for the change in activation energy of the faster exchanging type of water "B" at (or just below) 0°C . If "B" is a layer of water which is comparatively free to move about on the clay surface (either as first suggested a layer of water only in close proximity to the clay surface on one side, or water on the outer surface of the clay) then there are two possibilities for the way in which it is bound. Provided there is sufficient room on the clay surface it would be possible that the water molecules are not very close to one another. In other words there may be individual water molecules here and there, that are only attached in one way, namely by a Hydrogen bond to one of the Oxygen atoms of the clay surface. That is they are not sufficiently close together to be Hydrogen bonded to each other. Thus these water molecules are only very loosely attached to the clay surface, and so would exchange very readily with any water vapour present. However if what water molecules there are present are close together they could be linked into rings with one another as described before for the majority of water present ("C"). Thus, if this was the case, then the water molecules would

be expected to exchange more reluctantly than if they were on their own, and their activation energy would be expected to be similar to that for the rest of the water "C".

On the basis of the above suggestions the change in activation energy at (or just below) 0°C can be explained by assuming that above 0°C the water molecules are only loosely bound and so have a very small activation energy (as observed). However as the temperature falls below 0°C the water molecules present are "frozen" into an array similar to the rest of the water. Then the activation energy would be expected to be similar to that observed for the rest of the water. The actual value for the activation energy of "B" from 0°C to -21.3°C is 8,500 calories which is reasonably close to the value obtained for "C" namely 9,800 calories. If the actual temperature for the change in activation energy (that is the temperature at which "B" "freezes") was lower than 0°C then the activation energy would have a slightly higher value.

If this explanation for the change in activation energy is correct then it is difficult to see how "B" could be water on the outside surface of the clay. This would necessitate the water molecules being relatively free of one another above 0°C and this does not seem possible as there has to be 5-10 layers to account for the amount of water present.

If the water molecules of the type of water "B" are actually singly Hydrogen bonded above 0°C , then the specific rate constant for this type of water might be expected to be similar to that of Terylene. Terylene has a number of sites on which water Molecules could be adsorbed with

no possibility of them being Hydrogen bonded in more than one direction. The specific rate constant for the only type of water observed on Terylene has been shown to be 0.53 hours^{-1} at 0°C (19) which is at least comparable with the average values obtained in the present work viz:

Hydrogen Montmorillonite k_b (average) = 1.48 hours^{-1} at 0°C .

Potassium Montmorillonite k_b (average) = 0.928 hours^{-1} at 0°C .

Studies by Mason (20) on the formation of snow crystals in clouds which melt to form raindrops, showed that Montmorillonite could be used for "seeding" clouds, that is providing nuclei for the condensation of very small ice-crystals which will then grow in size. It was found that Montmorillonite was not effective unless the temperature was -25°C (or lower). However after particles of Montmorillonite had been cooled to this temperature and the ice-crystals formed around them evaporated in a dry atmosphere, the resultant particles were then effective at about -10°C . In the light of the data obtained on Montmorillonite at 0°C and -21.3°C a possible explanation of this phenomenon is that at about -25°C the water molecules on Montmorillonite undergo another change. If the Hydrogen bonds between the first layer of water molecules and the clay surface were to alter in length this would cause the hexagonal rings of water molecules to pucker so that the four Hydrogen bonds to the water molecules would adopt a tetrahedral configuration. If this was so this puckering would apply to both types of water "B" and "C" as at this temperature they would both have the same configuration. Thus, with the surface of the Montmorillonite consisting effectively of a layer of ice, droplets of water in the surrounding atmosphere would

readily condense on the surface and so an ice-crystal would grow. Once the water molecules on the Montmorillonite adopted such an ice-like structure it is conceivable that this arrangement would be fairly stable, and thus it would only be necessary to cool the surrounding water droplets to -10°C before they would condense on the ice-like Montmorillonite surface.

C. Studies of Lithium, Magnesium and Barium Montmorillonites

From the experiments performed on the above-mentioned clays it appears that Magnesium and Barium ions are not hydrated, at least at 78% relative humidity. In Lithium Montmorillonite the ions appear to be hydrated at least at 18.7% relative humidity and probably also at 78% relative humidity. However more work needs to be done on these clays before any definite conclusions can be drawn.

A study of the amounts of water adsorbed onto all the various clays studied at 78% relative humidity (see Table II p.41) supports the theory that the slower exchanging type of water "C" is between the silicate layers in the clay. As it is generally accepted ⁽¹⁾ that the exchangeable cations are between the silicate layers, the amount of "C" would be related to the charge and size of these cations, as the greater the size/unit charge the less room there would be left for water molecules. It can be seen that Hydrogen, the smallest cation, has most water associated with it, followed by Lithium the next smallest. Barium and Magnesium come next followed by Potassium. The Barium and Magnesium clays have more water than Potassium because, as they are divalent ions, there is only half as many of them present as there are Potassium ions.

D. Allophane

The Differential Thermal Analysis curve of Allophanes ⁽²¹⁾ show a broad endothermic peak in the region 100° to 200°C . From a study of a number of Allophanes in volcanic ashes of different ages ⁽²¹⁾ it is believed that for early stages of Allophane formation this peak is a composite of two different peaks. The first peak at about 125°C is due to hydrous silica and is observed in the Differential Thermal Analysis pattern of Silica Gel. The second endothermic peak at about 200°C is given by clays containing amorphous hydrous alumina, and also by some samples of artificial colloidal hydrous alumina. It is assumed that the existence of only one broad peak in more mature stages of Allophane is evidence that the silica and alumina are not discrete in these clays. Even mature Allophane, however, because of its aluminosilicate composition will have surface sites associated with both silicon and aluminium. From the above discussion it seemed likely that samples of Allophane would have two different types of water attached to them and that there would be significant differences in the specific rate constants due to the two stages of maturity of the samples.

As shown in Table III (p.42) results of this type were achieved but further work including replication and comparison with measured values of alumina and silica gels and related substances would be required before the results could be satisfactorily considered for interpretation.

SUMMARY

A new technique is developed for the study of adsorption onto surfaces by the use of simultaneous exchange reactions at equilibrium. This technique is applied to a study of the Montmorillonite - water system. The Allophane - water system is also studied briefly.

Montmorillonite samples saturated with Potassium and Hydrogen ions were studied at various relative humidities at 0°C and from the data obtained phase diagrams were prepared for each species. It was found that there were two different types of water on both the Hydrogen and Potassium Montmorillonites and that a third type of water appeared on the Potassium Montmorillonite above 80% relative humidity. It is believed that this third type is associated with the Potassium ions present.

Hydrogen Montmorillonite was also studied at different temperatures, and activation energies for each type of water present obtained.

Montmorillonite samples saturated with Lithium, Barium and Magnesium ions were studied briefly.

Two samples of Allophane derived from volcanic ashes of different ages were studied. It was found that both samples had two different types of exchangeable water.

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