# THE HYDRATION AND SWELLING OF CLAY MINERAL SYSTEMS

A Thesis Submitted
by
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# PREFACE

The work described in this thesis was carried out in the Department of Agricultural Chemistry, University of Adelaide, under the supervision of Dr. J. P. Quirk, Reader in Soil Science.

Except where due reference is made in the text, the thesis contains no material previously submitted for a degree in any University either by the author or any other person and represents the author's unaided work.

L. A. G. Aylmore
May, 1960

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# INTRODUCTION

The clay minerals and their relationship with water have attracted increasing interest in recent decades due to their considerable importance in many fields of study and because of the light that such studies can throw on the fundamentals of surface phenomena.

From an agricultural point of view the stability of soil aggregates to processes of wetting and drying and also to the mechanical stress applied during cultivation is of considerable importance. In addition water retention and permeability are important soil properties. Soil aggregates consist of a porous mixture of particles ranging in size from coarse sand to fine clay. Of these the clay fraction due to its small particle size and consequent large specific surface area, is of most importance in determining the physico-chemical reactions of the soil. Consequently many practical problems in agriculture are dependent for their solution on a better understanding of the interaction between water and the soil clay minerals.

Similarly soil engineering studies are concerned with the consolidation and shear strength of the soil-water mass and thus are fundamentally dependent to a certain extent on the clay-water interaction as well as mechanical particle to particle interaction. Much of the work carried out in this field has been empirical but lately the importance of fundamental knowledge concerning clay-water interactions has been more fully realised.

Additional interest has arisen due to the applications found for the clay minerals in the ceramic, oil drilling and other industries and their general usefulness as colloidal materials.

The adsorption of water on solid surfaces and the nature of the reaction between a charged surface and the ions in a solution in contact with it are determined by fundamental atomic and molecular forces. Soil clay minerals consist for the major part of negatively-charged, plate-shaped particles of colloidal dimensions. Consequently an elucidation of the behaviour of clay-water systems in terms of these forces can provide information of interest to many fields of science concerned with surface and interface phenomena.

In this thesis the hydration and swelling of a range of common clay minerals have been studied in relation to the clay species , specific surface area, exchangeable cation, electrolyte concentration and hydrostatic suction of the surrounding solution and the structural characteristics of the clay mass. This has been done using samples of the clays compressed into small cylindrical cores to facilitate experimental determinations.

The aim of this investigation was to establish precise experimental data on which swelling theories based on Gouy-Chapman diffuse double layer considerations could be thoroughly tested and to provide a general overall picture of the behaviour of clay-water systems. Both monovalent (sodium, potassium) and divalent (calcium, magnesium) systems have been studied. Although theoretical considerations are simpler for monovalent systems, the situation where calcium is the exchangeable cation warrants particular attention as this is the circumstance most frequently encountered in natural soils. It was hoped that such work would establish a connection between the physical swelling of clays in general and the intra-crystalline swelling of the montmorillonites to which X-ray diffraction techniques have been applied.

The thesis is divided into five sections. Section 1 contains a general review of the relative literature. In Section 2 the preparation of the clay materials is described and a number of experimental techniques have been used to examine the clay core systems in terms of their physico-chemical and structural characteristics. Although the nitrogen adsorption apparatus was not constructed and the electron micrographs were not obtained until the majority of the swelling work had been completed, the results of both are presented first as a basis for the discussion of the swelling results. In the light of probable structural configurations of the clay-water mass the analysis of solution content-suction data in terms of film thickness developed on the clay surface is briefly discussed in Section 3. In Section 4 a number of experimental techniques have been used to enable solution content-suction relationships for the different clay minerals to be obtained. The results are discussed in terms of the results obtained in Section 2 and also in terms of the possible models discussed in Section 3. Finally in Section 5 the general conclusions are summarized and discussed.

## SECTION 1

## GENERAL REVIEW OF LITERATURE

### 1. CRYSTALLINE STRUCTURE OF THE CLAY MINERALS.

Previous to about 1930 comparatively little was known concerning the structure of the common clay minerals and they were generally considered to be amorphous hydrous aluminium or magnesium silicates. The application of X-ray diffraction techniques to the study of clays provided conclusive evidence of their crystalline nature and rapidly led to their classification into different groups in terms of their crystalline structure.

The more commonly occurring clay minerals are those of the kaolin, illite and montmorillonite groups and two basic structural sheets are involved in the formation of the plate like crystals of these minerals.

The silicate sheet consists of silicon tetrahedrally co-ordinated with oxygen atoms or hydroxyl groups and the tetrahedrons arranged in a hexagonal network which is repeated indefinitely to form a sheet of composition $SiO_6(OH)_4$.

The second sheet consists of aluminium atoms in octahedral co-ordination between two layers of closely packed oxygens or hydroxyls.

The exchange capacity of the clays results mainly from the difference in valence of trivalent aluminium substituting for tetravalent silica in the silicate sheet, or of divalent magnesium or ferrous iron substituting for trivalent aluminium in the aluminate sheet. Each such substitution leaves one negative charge upon the lattice which has to be compensated by free positive ions upon or near its surface.

In the kaolin or 1:1 lattice type group, one silica and one alumina sheet combine to form the basic repeat unit, with the oxygen atoms at the apicies of the silica tetrahedra being shared by both sheets. This structure is represented by Figure 1. (Gruner, 1932).

The hydrated mica or illitic group has a 2:1 lattice structure consisting of an octahedral sheet sandwiched between two silica tetrahedral sheets. The tips of the tetrahedrons in each silica sheet point towards the centre of the unit and are combined with the octahedral sheet in a single layer. The silicate layers in illitic clays always carry a charge due to the substitution of trivalent aluminium for tetravalent silica and this charge deficiency is balanced by potassium ions partially embedded in the silicate sheet and providing such strong electrostatic attractions between adjacent sheets that these ions are not exchangeable.

The montmorillonite or expanding lattice group has essentially the same repeat unit as the illites but possesses considerably less charge on the silicate sheets. Exchangeable cations occur between the silicate sheets and the outstanding feature of this group is the ability of water and other polar molecules to enter between the unit layers causing the crystal lattice to expand in the direction of the C axis.

The lattice structure of both illite and montmorillonite are similar to that of pyrophyllite shown in Figure 2. (Pauling, 1930).

More general reviews and detailed descriptions of the crystalline structures of the clay minerals as determined by numerous

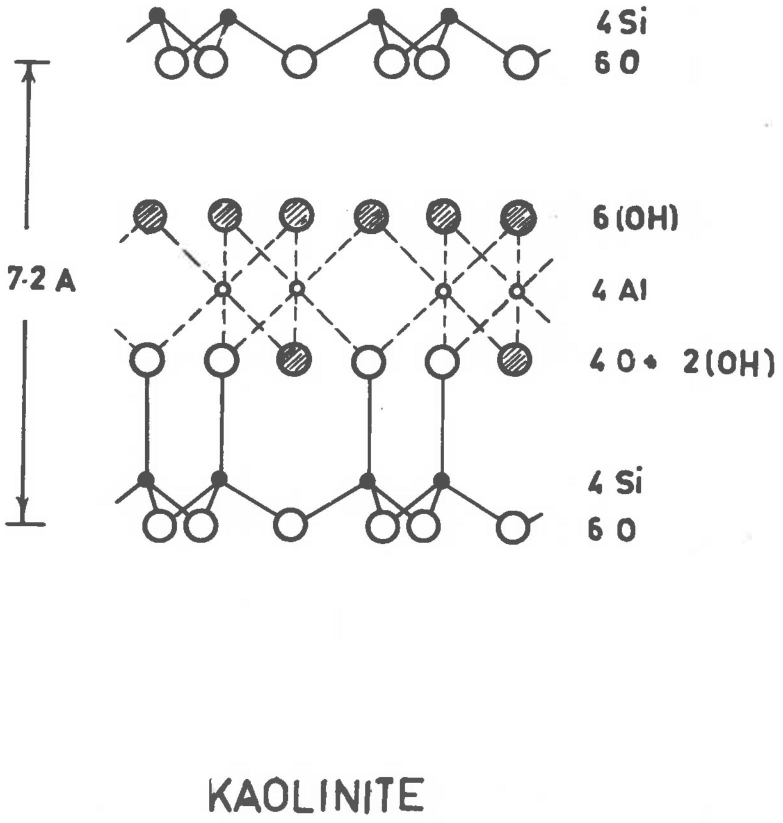


FIGURE 1.

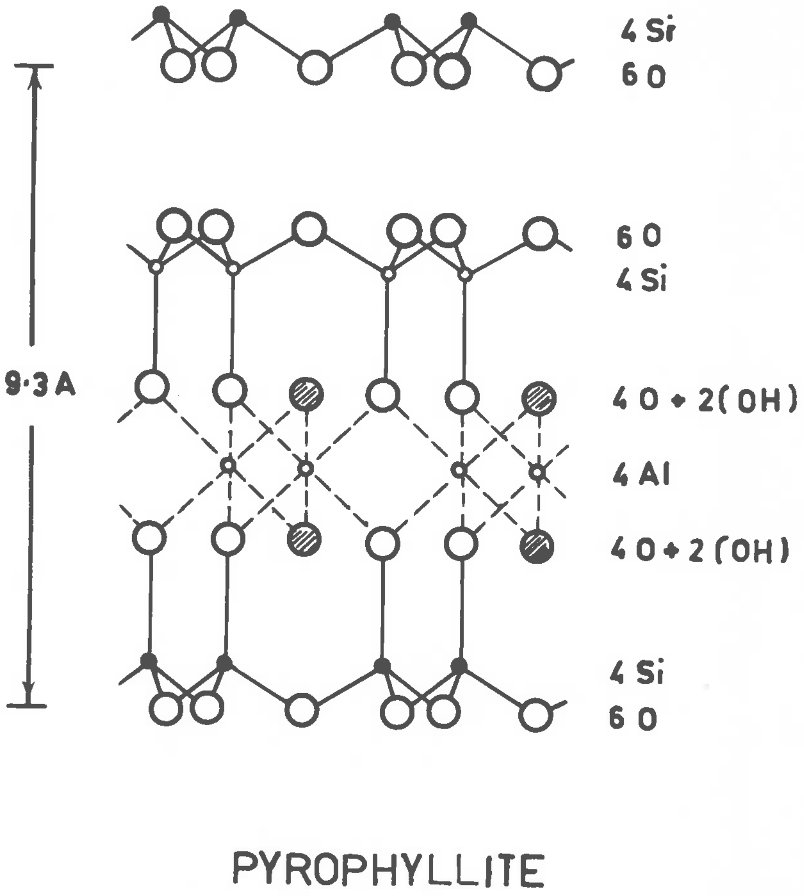


FIGURE 2.

workers notably Pauling (1930), Gruner (1932), Jackson and West (1930, 1933), Hofmann, Endell and Wilm (1933), Hendricks et al (1936, 1938), Marshall (1935), Maegdefrau and Hofmann (1937), and Brindley et al (1946, 1951) have been given by Marshall (1949) and Grim (1953).

## 2. CLAY-WATER RELATIONSHIP

Since the confirmation by X-ray investigators of the crystalline nature of the clay minerals, much work has been done in an attempt to elucidate the factors involved in the uptake of water and the consequent swelling exhibited by these minerals. The results of this work have shown that there are several mechanisms involved, their applicability depending on the state of hydration and expansion of the clay matrix. For convenience water sorbtion can be divided into the following categories.

1. Surface Adsorption and Hydration of Cations.
2. Capillary Condensation.
3. Swelling.

### 2.1 Surface Adsorption and Hydration of Cations.

Water vapour adsorption has received considerable attention from numerous workers over the past forty years. The early work of Thomas (1921, 1924), Puri, Crowther and Keen (1925) and Alexander and Haring (1936) on the adsorption of water vapour by soils and soil colloids of rather indefinite composition, indicated that the amount of water vapour adsorbed by a soil increased with the vapour pressure, decreasing temperature and specific surface area. Falconer and Mattson (1933), Baver and Winterkorn (1935) and Lutz (1935) showed that the exchangeable cations also influenced the water uptake of clays.

Since the initial water taken up is undoubtedly associated with the exchangeable cations or adsorbed directly onto the clay surface the attention of soil and colloid scientists has in recent years been focussed on a number of adsorption equations.

### 2.1.1 Theories of Adsorption

Five isotherm types have been distinguished by Brunauer (1943) as occurring in physical adsorption. These are shown in Figure 3.

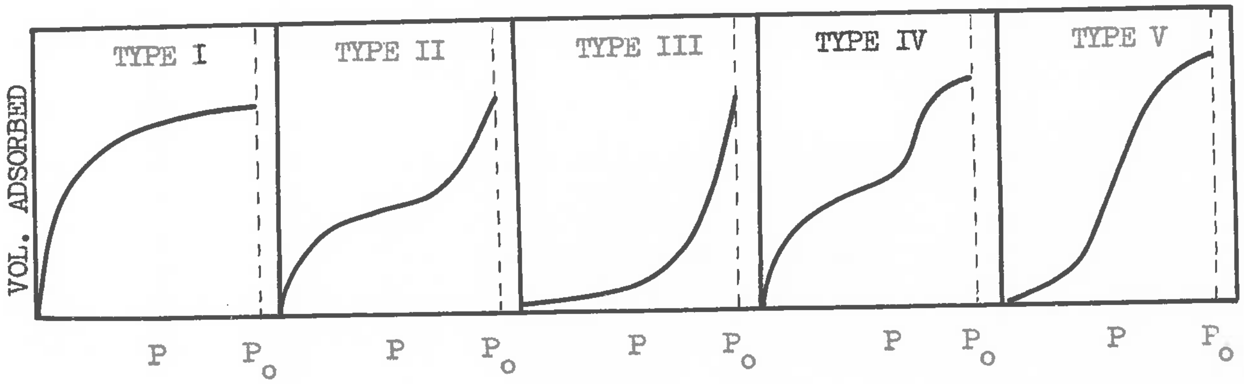


FIGURE 3

At the present time most theories of adsorption are based on the assumption that a unimolecular layer is formed first with subsequent multimolecular layer formation as the gas or vapour pressure is increased. The main difference in the theories lies in the assumption as to the nature of the adsorbate in the film.

Langmuir (1918) assumed that the adsorbed layer was unimolecular and that a dynamic equilibrium was set up in the adsorption system between the rate of condensation of a gas on the surface of the adsorbent and the rate of evaporation. The Langmuir isotherm equation is written:

$$\frac{p}{v} = \frac{1}{Bv_m} + \frac{p}{v_m} \qquad (1)$$

where v is the quantity adsorbed at pressure p, $v_m$ is the amount required to form a monolayer and B is a constant for any particular temperature. This equation is limited to giving approximations to only Type I isotherm of Brunauer's classification.

In 1938 Brunauer, Emmett and Teller by a generalization of the Langmuir monolayer adsorption theory to multilayer formation derived the equation :

$$\frac{p}{v(p_o-p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \cdot \frac{p}{p_o} \qquad (2)$$

for adsorption on a free surface where v, $v_m$ and p are as before, $p_o$ is the saturation vapour pressure and c is a constant related to the heat of adsorption of the first layer ($E_1$) and the heat of liquefaction ($E_L$) by the relation :

$$c = \frac{a_1 b_2}{b_1 a_2} \cdot e^{(E_1 - E_L)/RT} \qquad (3)$$

in which $a_1$, $a_2$, $b_1$ and $b_2$ are rate constants.

The main fundamental assumption in the derivation of equation (2) is that the first layer of molecules is adsorbed at a particular energy and that all subsequent layers are adsorbed at an energy equal to that for the condensation of the pure liquid. This is a linear equation and the plot of $\frac{p}{v(p_o-p)}$ against $p/p_o$ should give a straight line if the theory is obeyed. The intercept is $\frac{1}{v_m c}$ and the slope $\frac{c-1}{v_m c}$ so that the two constants c and $v_m$ can be obtained from experimental data.

For limited or restricted multilayer formation e.g. in small pores of capillaries, the equation derived (Brunaner, Deming, Deming and Teller, 1940) is

$$v = \frac{v_m cP\left[1-(n+1)P^n + nP^{n+1}\right]}{(1-P)\left[1+(c-1)P - cP^{n+1}\right]} \tag{4}$$

where $P = \frac{p}{p_o}$ and n is the maximum number of adsorbed layers.

For n = 1 the equation reduced to

$$v = \frac{v_m cP}{1+cP} \tag{5}$$

which is identical with the Langmuir equation.

For $n = \infty$ equation (2) is obtained. However for values of n greater than 3 or 4 equation (2) is a fair approximation to equation (4) providing c is considerably greater than unity.

Equation (2) has also been derived by Hill (1949) from statistical mechanical reasoning using similar assumptions to Brunaner, Emmett and Teller.

The Multimolecular Adsorption or B.E.T. Theory accounts satisfactorily in a general way for the five isotherm types described by Brunaner and is the most widely applied theory in use at the present time. For n = 1, Type I isotherm are obtained and for n > 1, Type II or III isotherm are obtained, according to whether $E_1$ is > or < $E_L$. In order to explain Type IV and V isotherms, capillary condensation is usually postulated.

$$\frac{p}{v(p_0-p)} = \frac{1}{V_m c} + \frac{c-1}{V_m c} \cdot \frac{p}{p_0}$$

In practice equation (2) is found to be obeyed very closely by most adsorbates over the range $p/p_o = 0.05$ to $0.35$.

From the assumption that the adsorbent polarised the molecules of the first layer of adsorbate and that this polarization was transmitted from one layer of molecules to the next with decreasing magnitude Bradley (1936) derived the three constant equation

$$\log \frac{p}{p_o} = K_2 K_1^{\,x} + K_3 \qquad (6)$$

for adsorbed molecules with large permanent dipoles. $x$ is the mass of gas adsorbed, $p$ the vapour pressure and $p_o$ the saturation vapour pressure.

Harkins and Jura (1944) combined the empirical two dimensional equation of state for a condensed monolayer with the thermodynamic adsorption equation derived by Gibbs for adsorption on solid surfaces and obtained the equation :

$$\ln \frac{p}{p_o} = B - \frac{A}{x^2} \qquad (7)$$

in which A and B are constants, $\frac{p}{p_o}$ is the relative pressure and $x$ the mass of the adsorbate.

### 2. 1.2 Water Vapour Adsorption on Clay Surfaces

The possibility of using these equations in conjunction with water vapour adsorption isotherms to provide an estimate of the surface areas of soils and soil colloids and to examine the effect of exchangeable cation has been investigated. The B.E.T. equation (2) in particular has received attention from numerous workers.

In a series of papers Keenan, Mooney and Wood (1951, 1952) applied the B.E.T. Theory to the adsorption of water vapour by homoionic kaolinite and montmorillonite clays. They pointed out that the term monolayer was not strictly correct for polar molecules in the presence of exchangeable cations but that the fundamental assumption of the B.E.T. Theory probably still applied with the parameter $v_m$ representing a well defined quantity characteristic of a given system. A correlation of their results with surface areas determined by low temperature nitrogen adsorption demonstrated that the effect of a particular cation on water adsorption was determined by both its size and charge. For kaolinites the monovalent alkali metal ions showed a decreasing effect with increasing size in the order Na > K > Rb > Cs as would be expected, the smaller ions having a greater affinity for water of hydration. Lithium ions were considered to be stearically hindered from adsorption by accommodation in lattice holes in the clay surfaces. The divalent ions with their double charge were again more strongly hydrated; their effect also decreased with increasing size in the order Mg > Ca > Sr > Ba.

In the case of the montmorillonite clays the application of the B.E.T. Theory was further complicated by the ability of the polar water molecules to enter between the unit lamellae composing the clay crystals. The adsorption isotherms for the montmorillonites were found to be very dependant on the initial water content at which the adsorption was begun and these workers concluded that reproducible adsorption data on montmorillonites could not be obtained for this reason. For the desorption data the B.E.T. parameter $v_m$ was interpreted as indicating the adsorption when only one layer of molecules occurred between each pair of lamellae plus the monolayer on the external surfaces. The total surface areas calculated on this assumption were in general agreement with those calculated from the constitution of the unit cell.

Coates and Hatch (1953) developed the B.E.T. equation using a thermodynamic approach and showed the constant c to be related to the standard Gibbs free energy of adsorption (standard adsorption potential) of the first layer of molecules by the equation :

$$c = e^{(F_1^o - F_2^o)/RT} \tag{8}$$

in which $F_1^o$ is the standard Gibbs free energy of adsorption of the gas on the bare solid surface and $F_2^o$ is the standard Gibbs free energy of condensation of the adsorbate. Using Alexander and Haring's (1936) data these workers indicated the usefulness of $F_1^o$ as a means of characterizing the surfaces of soil colloids since it is determined only by properties of the adsorbate and the nature of the surface.

Orchiston (1953) compared the B.E.T., Bradley and Harkins and Jura adsorption theories and derived three semi-empirical equations to enable specific surface areas of soils to be determined at 25°C from a single adsorption point on the isotherm. Using adsorption isotherms he found that for a number of New Zealand soils the monolayer was complete at a relative vapour pressure of 0.21. Later working with a montmorillonite from Yavapai County, Arizona, he (1954, 1955) found that the monolayer was completed at relative vapour pressures ranging from 0.16 to 0.34 depending on the exchangeable cation present. For an illite and kaolinite the monolayers were completed at approximately 0.25 and 0.14 relative pressure respectively. In the case of the montmorillonite a linear relation between the heats of hydration of the cation and the c parameter in the B.E.T. equation was demonstrated thus emphasising the predominant role of the cation in the adsorption process.

Using the data of a number of previous workers Quirk (1955) evaluated the surface areas of clays determined by applying the B.E.T. theory to water vapour sorption data and from the retention of ethylene glycol (Dyal and Hendricks, 1950). He concluded that such measurements were unreliable due to the polar molecules being preferentially adsorbed around the cation sites and that the surface area determined would therefore obviously depend on the surface density of charge. He suggested that the water retained by a calcium saturated soil or clay at a relative vapour pressure of 0.20 would provide just as useful an estimate of the surface area as that obtained by application of the B.E.T. theory to water vapour adsorption.

X-ray diffraction techniques have been used to study the variation in interlamellar spacing of the expanding lattice clays with the amount of water vapour adsorbed, commonly referred to as crystalline swelling. Bradley, Clark and Grim (1937) using a hydrogen montmorillonite obtained by electrodyalysis of a Wyoming bentonite concluded that the spacing did not change continuously with water content but in a discrete stepwise fashion, only spacings corresponding to integral layers of water molecules between the sheets being found. This conclusion was supported by the results of Hendricks, Nelson and Alexander (1940) who determined the water adsorption, c-axis spacing and corresponding differential thermal curves at various relative humidities for montmorillonite saturated with various cations. The results of Mooney, Keenan and Wood (1952) and Norrish (1954) showed this stepwise hydration of the montmorillonite lattice to be quite general although dependant on the hydration energy of the cations. When the clay carried an adsorbed ion that hydrates it has been suggested (Mering, 1946; Walker, 1951) that the development of discrete monomolecular water layers is prevented by the co-ordination of water of hydration about the cation.

### 2.1.3. Nature of the Adsorbed Water.

Opinions have been varied as to the state of the first layers of water molecules adsorbed on a clay surface but it is generally accepted that it is different to that of the normal liquid and that some form of structural order exists. There is strong evidence from colloid science to suggest that an adsorbed water layer with highly oriented molecules does exist on the surface of colloid particles, but the actual thickness has been estimated as being from a few angstroms to many thousands of angstrom units (McBain, 1950; Kruyt, 1949). However, it must be remembered that the change from bonded water to free water would not be abrupt. The estimated thickness would therefore depend on an arbitrary selection of the boundary between free and bonded water.

The Hendricks and Jefferson (1938) concept visualized the initial water molecules as arranged in a hexagonal network bound to the surface of the clay by the attraction between those hydrogen atoms not involved in bonding within the net and the surface oxygen layer of the clay mineral unit. This hypothetical structure was based partly on Bernal and Fowlers (1933) concept of the tetrahedral charge distribution of a water molecule in liquid water.

Macey (1942) has suggested that the initially adsorbed water has the structure of ice since the oxygen atoms exposed at the surface of the clay minerals possess a similiar arrangement to that of ice.

These concepts have been criticized since they neglect the probable influence of the adsorbed cations which must be in close proximity to the clay surface.

Mathieson and Walker (1954) carried out a single crystal X-ray analysis of an hydrated magnesium vermiculite (d(001) = 14.8 Å). The vermiculites which bear a striking similarity to the montmorillonite clays both in structural configuration and dependance of intermlamellar spacing on the exchangeable cation, have the advantage experimentally that comparatively large single crystals can be obtained thereby facilitating X-ray investigation. Mathieson and Walker located the exchangeable magnesium cations in a plane midway between the silicate layers and from their results they concluded that the interlamellar water was arranged in two sheets of hexagonal close packed water molecules, bound to the silicate sheets by hydrogen bonding, whose relationship to each other was determined by the requirement of an octahydral co-ordination of the water molecules around the cation.

More recently Low (1959) has provided experimental evidence indicating a density less than unity for water held on the planar surfaces of montmorillonite clay particles and favours an explanation in terms of the tendency of each water molecule to bond itself tetrahedrally to four neighbouring water molecules as in ice. The polarizing influence of the negatively charged clay surface and possibly hydrogen bonding to it are considered to have a stabilizing effect on this "broken down ice structure". The adsorbed ions are considered as having a disrupting influence on this stabilization.

As suggested earlier the nature of the adsorbed water will undoubtedly vary considerably from the immediate vicinity of the clay surface to positions further out in the adsorbed film.

## 2.2 Capillary Condensation

The idea of condensation in small capillaries at pressures far below the saturation vapour pressure was first formulated by Zsigmondy in 1911 and since then this phenomenon has been generally accepted by most workers as playing some part in the sorption process. The fundamental equation usually employed is the Kelvin relation.

$$\ln \frac{p}{p_o} = \frac{2V\gamma \cos \theta}{rRT} \qquad (9)$$

where p is the equilibrium pressure, $p_o$ is the saturation vapour pressure, $\gamma$ is the surface tension and V is the molar volume of the liquid at temperature T, $\theta$ is the contact angle and r is the Kelvin radius.

The use of the Kelvin equation to obtain comparative data usually involves the following assumptions.

(1) Either the adsorption or desorption branch of the isotherm represents an equilibrium across a concave meniscus according to the Kelvin equation.

(2) Adsorption is entirely due to capillary condensation.

(3) The physical properties of the adsorbed layer are identical with those of the bulk liquid adsorbate.

(4) All pores are cylindrical.

By expressing the isotherm as volume of liquid adsorbate adsorbed versus relative pressure, a pore volume - equivalent cylindrical radius curve can be constructed.

Both Zsigmondy, and later Foster (1932) considered that capillary condensation did not occur until after the initial formation of an adsorbed layer. In recent years opinions seem to favour a combination of layer formation and capillary condensation. (Foster, 1948; Barrett, Joyner and Halenda, 1951).

The applicability of the Kelvin equation to pores of molecular dimensions has been open to some doubt since at these dimensions the values of $\gamma$ and V, both statistical quantities may vary considerably from those for the liquid in bulk. However, Foster (1948) has expressed the view that for comparative purposes in the adsorption of two liquids good agreement is found down to pore radii of about 8 Å.

A number of workers (Foster, 1932; Cohan, 1938) have maintained that a characteristic of capillary condensation is the appearance of hysteresis in the sorption isotherms denoting that for the same volume of vapour adsorbed, the equilibrium pressure of the adsorption side is higher than that of the desorption side.

## 2.3 Hysteresis.

The phenomenon of hysteresis in the vapour pressure - liquid content relation has long been of considerable interest to workers in many fields.

The first successful explanation of irreversible hysteresis was given by Zsigmondy (1911) in terms of the capillary condensation theory by assuming incomplete wetting of the pore walls by the vapour during adsorption, due to the presence of impurities such as air adsorbed on the walls, giving rise to an increase in the angle of contact during adsorption.

Reversible hysteresis has usually been regarded as evidence for the presence of pores and early explanations of it were generally centered on some facet of the geometry of the system.

Haines in 1930 suggested that the cellular nature of the soil pore space imposed a quantum-like character on the moisture changes during wetting and drying and that a fundamental difference in the mechanisms involved in filling and emptying a cell gave rise to hysteresis. Smith (1936) considered hysteresis to arise from the isolation during the dehydration process of discrete liquid masses due to the configuration of the pore space. During hydration these identical configurations could remain unsaturated for the same vapour pressure.

A similiar delay in desorption was envisaged by Kraemer (1931) and later developed by McBain (1935): Rao, (1941) and Katz, (1949). This so called "ink bottle" theory postulates that the water content is determined by the radius of the body of a bottle shaped pore on wetting and by the radius of the neck on drying from saturation.

Foster (1932) developed an "open pore" theory in which he considered the irreversible process to be the formation of the meniscus prior to capillary condensation. During adsorption the formation of a meniscus in a pore and the corresponding occurrence of capillary condensation would occur only when the adsorbed film is thick enough to block the pore at its narrowest point. At this stage the wider pores would still only have adsorbed films. Thus the ascending branch of the loop would correspond to adsorption and capillary condensation occurring simultaneously. Dehydration from saturation with a meniscus in every pore would then be determined solely by capillary condensation.

Other workers (Cohan, 1938; Coolingh, 1939) have suggested that the meniscus of a liquid condensed in a capillary has a cylindrical shape on adsorption and a spherical shape on desorption. This leads to the result that the equivalent radius of curvature during the adsorption process is twice as large as during desorption.

The theories reviewed so far are alike in that they all require the presence of both vapour and liquid in the pore space to account for hysteresis. However, both irreversible and reversible hysteresis have been observed in expanding porous systems with complete liquid saturation throughout the adsorption and desorption cycle. Schofield (1938) in discussing the early work of Haines (1923) on clay blocks pointed out that hysteresis occurred when there was no air in the system and hence none of the above theories would apply. This observation was confirmed by Croney and Coleman (1954) and later Holmes (1955). Holmes found from measurements of the water uptake and swelling of moulded clay cores that the lower degree of saturation for the wetting curve could only account for a small part of the observed difference between the two branches of the water content-suction curves. He concluded that most of the hysteresis was associated with plastic readjustments of the clay particles relative to their neighbours as suggested by Schofield (1935). A similar idea has recently been elaborated by Barkas (1946) from studies of the hysteresis in a two phase system of wood gel and water.

Collis-George (1955) compared the hysteresis moisture - energy relationship for wetting and drying of a constant structured sintered glass system with that of a colloidal sodium montmorillonite gel. He suggested that for pores that empty the major part of the phenomenon was due to the geometry of the system and about 6% due to angle of contact theory, whilst for non emptying pores which could expand and contract a third mechanism based on the interaction of colloidal particles was necessary.

A general theory to explain hysteresis phenomena has been postulated by Everett and Whitton (1952) in which hysteresis is attributed to the existence in a system of a very large number of independant domains, at least some of which can exhibit metastability.

## 2.4 Swelling.

The adsorption of water between clay plates causes them to move apart resulting in a overall change in the volume of the clay-water system referred to as swelling. The extent to which the water film on a clay surface develops has been shown to depend on such factors as the nature of the exchangeable cation, surface density of charge, electrolyte concentration and the suction applied to the external solution. For any system of particles in equilibrium there is a balance between the repulsive forces tending to separate them and the attractive forces tending to compact them. The nature of this equilibrium in clay-water systems and the origin of the repulsive and attractive forces operative has instigated considerable research both theoretical and experimental.

### 2.4.1. Repulsive Forces.

Soil clay particles carry a negative charge due to the ionic substitutions within the crystal lattice. Overall electroneutrality is maintained by the presence of an excess of positive counterions in close proximity to the clay surface. When immersed in a liquid medium the coulombic attraction of the clay plates for the counterions is opposed by the dispersive action of thermal motion giving rise to a diffuse distribution of the counterions. Negative anions and positive cations of any dissociated electrolyte present will be respectively repelled from and attracted to the clay surface giving rise to similar diffuse distributions.

The nature of this distribution was first investigated by Gouy in 1910 and later by Chapman (1913) in order to obtain the relationship between the surface density of charge on the solid and the potential across the diffuse component of the electric double layer. In the Gouy-Chapman theory the average concentration of the ions at a given point is assumed to follow the Boltzmann distribution law.

$$n_j = n_{jo} \exp.\left(- \frac{v_j e \psi}{kT}\right) \qquad (10)$$

where $n_j$ equals the number of ions of type j per $cm^3$ at an arbitrary point in the diffuse layer where the potential is $\psi$ and $n_{jo}$ is the corresponding concentration at a point far removed from the solid surface where $\psi = 0$. $v_j$ is the valence of the ion, e is the electric charge or minus the charge of the electron depending on the sign of the charge on the ion, k is the Boltzmann constant and T the absolute temperature.

The relation between the electric potential $\psi$ and the space net charge density $\rho$ is given by the Poisson equation :

$$\Delta \psi = - \frac{4\pi\rho}{\epsilon} \qquad (11)$$

where both $\psi$ and $\rho$ are functions of the co-ordinates x, y and z and $\epsilon$ is the dielectric constant of the medium. $\Delta$ is the Laplace operator.

For a direction perpendicular to the surface this equation reduces to

$$\frac{d^2 \psi}{dx^2} = \frac{-4\pi\rho}{\epsilon} \qquad (12)$$

Combining equations 10 and 12 leads to the fundamental Poisson - Boltzmann differential equation

$$\frac{d^2\psi}{dx^2} = \frac{-8\pi n v e}{\epsilon} \sinh \frac{v e \psi}{kT} \qquad (13)$$

since $\rho = (v^+n^+ + v^-n^-)e$

Solutions of this equation for the case of a single clay particle surface are obtained by integrating between limits corresponding to $x = 0$ and $x = \infty$. The electric potential between two interacting plane parallel surfaces is obtained by integrating between $x = 0$ and $x = \frac{d}{2}$ where d is the separation between the plates.

The theory developed by Gouy-Chapman ignores the finite dimensions of the ions in solution assuming them to be point charges capable of unlimited approach to the charged surface. In dilute solutions where the development of the diffuse layer is considerable the error due to this assumption is small. In more concentrated solutions however, values obtained for the concentration of ions near the surface are absurdly high in view of the finite dimensions of the ions.

Stern in 1924 suggested that the counterions could be divided into two parts : a layer of ions several angstroms thick adsorbed directly onto the clay surface and the remainder in a diffuse distribution as envisaged by the Gouy-Chapman theory. Within the Stern layer the electric potential is assumed to decline linearly as in the dielectric of a plate condenser. Thereafter the potential declines as for the Gouy-Chapman theory. For dilute solutions only a small part of the potential drop will occur in the Stern layer and the potential distribution approaches that of the Gouy-Chapman concept. For more concentrated solutions a larger proportion of the potential drop will occur in the Stern layer as the diffuse component is progressively compressed.

Langmuir (1938) pointed out that an additional repulsive force to the electrostatic repulsion of like charges was necessary to account for the stability of colloids and obtained approximate solutions of the Poisson-Boltzmann differential equation for the repulsive pressure between two charged surfaces arising from the osmotic activity of the ions in the intervening solution.

More recently a theoretical treatment based on the Gouy-Chapman diffuse double layer theory has been presented by Verwey and Overbeek (1948). In this the necessary repulsive force is regarded as arising from the interaction of the diffuse double layers associated with the individual clay particles.

From slightly different considerations Schofield (1946) arrived at a similiar solution of the Poisson-Boltzmann differential equation and derived an equation to describe the thickness of a liquid film adhering to a charged surface in terms of the charge density on the surface and the concentration of exchangeable ions at the outer boundary of the film. This equation is

$$X = \frac{2}{v\sqrt{\beta C_0}} \cot^{-1} \frac{2\sqrt{C_0}}{\Gamma\sqrt{\beta}} \qquad (14)$$

where X is either the thickness of the liquidfilm adhering to a single solid surface on which there are charged atom groups at surface density $\Gamma$, or half the thickness of a film between two such surfaces. In obtaining this equation it was assumed that ions of one kind only and of valence v constituted the diffuse component of the electric double layer and that these ions are in ideal solution. $\beta$ is a constant depending on the temperature and the dielectric constant. $C_o$ is the ionic concentration at the outer surface of the film on one surface or that in the centre of the film between two surfaces. It was considered that the excess hydrostatic pressure acting on the film in equilibrium with the bulk liquid at the same height was $RTC_o$. Schofield compared the film thickness on glass and mica surfaces as measured by Derjaguin et al (1939, 1940) with that calculated using this equation. Excellent agreement was obtained between theoretical and experimental data for distilled water but for dilute sodium chloride solutions rather large deviations were observed.

Schofield (1947) also used diffuse double layer considerations to derive a relation between the negative adsorption of the repelled ions and their concentration in solution thus permitting the estimation of specific surface areas of clays from experimental data on negative adsorption.

At plate separations below about twenty angstroms the diffuse layer of counterions cannot form and alternate sources of repulsion must be found. Undoubtedly the hydration energy of the exchangeable cations themselves is one such source of repulsion and MacEwan (1948) has demonstrated that the surface adsorption of polar molecule is also of considerable importance in this respect. In general in clay-water systems the approach of one clay crystal to another is probably not close enough to significantly involve the Born repulsion arising from the mutual repulsion of ionic shells.

### 2.4.2 Attractive Forces.

The principal contribution to the attractive forces has been considered to come from the van der Waal's forces : universal forces acting between all pairs of atoms or molecules and varying inversely as the seventh power of the distance between them. These attractive forces are almost independant of surrounding atoms and are essentially additive so that the attractive force between two plates varies inversely as the third power of the distance between them. From London's (1930, 1931) theory of attraction between two atoms De Boer (1936) and Hamaker (1937) derived the equation

$$F = \frac{A}{6 \pi d^3} \qquad (15)$$

where F is the force in dynes/cm$^2$ and d the distance between two parallel plates.

One difficulty in this approach has been the uncertainty in the value of the constant A, values varying by nearly a thousand fold having been obtained by the Dutch (Overbeek and Sparnaay, 1954) and Russian (Derjagiun and Abricossova, 1954) schools respectively.

Overbeek and Sparnaay measured the small deflection of a spring produced by the attraction between parallel glass plates. A plot of their measured force against separation showed considerable scatter but obeyed approximately the above relation with the constant $A = 3.8 \times 10^{-11}$ ergs compared with a theoretical value of $10^{-12}$ ergs.

Derjaguin and Abricossova, using an electronically balanced knife edge microbalance, measured the attractive force between a plane quartz surface resting on one arm of the balance beam and a convex lens placed at a small distance above the plate. They claimed good reproducibility of results giving a value of $5 \times 10^{-14}$ ergs for the constant A. This value has since been confirmed by Prosser and Kitchener (1956) using an apparatus similar to that of Overbeek and Sparnaay but claimed to be of improved sensitivity.

It should be noted that in these experiments plate separations of the order of 1000 Å were used and extreme care was taken to eliminate electrostatic charges from the experimental surfaces. Prosser and Kitchener pointed out that the Casimir and Polder (1948) relation where the force is inversely proportional to the fourth power of the separation was more appropriate for separation of this order.

MacEwan (1948) pointed out that the van der Waals' forces calculated in this manner were far too small to account for the small separation equilibrium observed by X-ray workers in the crystalline swelling of montmorillonite and suggested the possibility of an electrostatic origin for the attractive forces at low plate separations. At separations below about 10 Å the Stern layers may coalesce to form a single layer of cations between the negative sheets. This would give rise to a condenser like system with a strong attractive force whose potential would increase uniformly with separation at a rate depending on the dielectric constant of the medium. This concept is strongly supported by Mathieson and Walker's (1954) location of the exchangeable magnesium ions in a plane midway between the silicate sheets of an hydrated magnesium vermiculite where the separation is about 5 Å.

The main difficulty in using this concept to calculate attractive forces arises from the uncertainty in the degree of dielectric saturation to be assumed for the intervening medium.

From a comparison of the calculated van der Waals' and electrical energies with the observed energy associated with an expansion of silicate sheets from a d(001) value of 12.4 Å to 15.4 Å Greene-Kelly (1953) concluded that electrostatic forces were largely responsible for the interlamellar attractions in mica like minerals. He calculated 160 me/100g. as the maximum charge density consistent with interlamellar expansion for montmorillonite type minerals and pointed out that this agreed fairly well with the observed swelling of the various layer lattice silicates.

At separations greater than about 10 Å MacEwan suggests that the electrostatic attractions would be reduced somewhat by the segregation of the cations into separate layers attached to each plate and finally with the complete formation of the diffuse double layer the force would become repulsive.

In studying the swelling of sodium and calcium Wyoming Bentonite Mering (1946) observed a 20 Å spacing in both cases and concluded that intracrystalline swelling did not proceed beyond 20 Å despite the increase in volume by about twenty times in the sodium case.

More recently Norrish and Quirk (1954) using low angle X-ray diffraction techniques have shown that while the d(001) spacing for calcium montmorillonite remains at 19 Å even in distilled water, sodium montmorillonite expands to 43 Å at a concentration of about 0.3 N and Norrish (1954) has shown that for hydrogen, lithium and sodium montmorillonites this expansion continues with spacing proportional to $\frac{1}{\sqrt{N}}$ where N is the normality of the solution. Norrish considers that the ratio of the repulsive to attractive potential for a particular ion is given by $\frac{U}{v^2}$ where U is the hydration energy and v the valence of the ion and has indicated that small variations in dielectric saturation would also effect swelling. Good agreement was obtained between this swelling index and the maximum crystalline swelling for a particular cation. The surface density of charge was also shown to be important in determining the maximum value of d(001) in crystalline swelling for expanding lattice minerals.

Once over the potential barrier the attractive force for sodium montmorillonite was shown by Norrish to decrease as the inverse 1.81 power of sheet separation instead of 4.4 as required by Verwey and Overbeek's (1948) treatment of van der Waals' forces. This slow rate of decay of attractive force even at large separations is strongly indicative of an electrostatic rather than a molecular origin.

### 2.4.3. Physical Swelling.

There is little satisfactory experimental data with which a comparison between the internal swelling of expanding lattice minerals and the film thickness developed on the external surfaces of clay crystals in general can be made. Attempts to correalate physical swelling data for clay materials with theoretical treatments have proved less conclusive than the more direct X-ray approach. The main difficulty experienced has been due to the fact that the water content of a clay mass at any particular water suction value has proved to be markedly dependant on its previous history.

The data obtained by Mattson (1932) for the water content-pressure relationship for montmorillonite gels over the pressure range 0.1 - 1 atmosphere was interpreted by Eriksson (1950) on the basis of a similiar solution of the Poisson-Boltzmann differential equation to those obtained by Schofield (1946) and Verwey and Overbeek (1948). Similarly Bolt and his co-workers (1955, 1956, 1957) starting with their materials in the gel state and applying progressively higher water suctions considered they had found reasonable agreement between the observed water film thickness-water suction dependance for monovalent systems and that to be expected from diffuse double layer theories. For divalent ion systems the agreement was less satisfactory. These workers calculated the water film thickness on the clay surface simply by dividing the water content by the specific surface area of the clay. For the montmorillonites the full theoretical surface area of approximately 800 $m^2/g$ was used for both sodium and calcium clays in these calculations. The magnitudes of the determined film thicknesses for illitic clays were somewhat larger than those theoretically predicted and to account for this, the presence of a "dead" volume of water attributed to the terraced nature of the clay particles had to be invoked. The maximum pressure used by these workers never exceeded 20 atmospheres so that their materials were always in a saturated state.

Earlier the results of Croney and Coleman (1954) and also Holmes (1955) had shown that at any one particular water suction it was possible for a clay mass to have a range of different water contents depending on its previous history and that in fact a disturbed clay mass described a series of hysteresis loops on repeated wetting and drying. This effect of terminal pressure on the decompression curve for clays in the gel state was also well illustrated by the results of Warkentin, Bolt and Miller (1957). Soil engineering workers (Lambe, 1953; Parry, 1959) have also been aware of the presence of this irreversible hysteresis in the water content-suction relationship, referring to consolidated and overconsolidated clays depending on whether the clay mass has been subjected to sufficient pressure to cause a decrease or an increase in volume on the application of shearing forces.

The results of Croney and Coleman (1954) and Holmes (1955) indicated that for a clay mass to describe what may be termed a final reproducible hysteresis loop it was necessary to dry it to its shrinkage limit. Presumably in this state the clay matrix has settled down to the situation where the clay particles are in a state of minimum potential energy with respect to each other. Hence in the present work the clay cores were first taken beyond their shrinkage limit, the relevant structural and physico-chemical characteristics determined and their behaviour on subsequent wetting and drying studied with the systems as clearly defined as possible.

## SECTION 2

## DETERMINATION OF PHYSICO-CHEMICAL AND STRUCTURAL CHARACTERISTICS OF CLAY SYSTEMS

### 1. DESCRIPTION OF CLAY MINERALS USED.

Initially the work was commenced with the following six clays :

Rocky Gully Kaolinite - from pallid zone of laterite, Rocky Gully, Western Australia.

Mercks I Kaolinite - obtained from Mercks Chemical Company, Germany, labelled DAB-6.

Grundite Illite - from County Grundy Illinois, supplied by Ward's Natural Science Museum, U.S.A.

Willalocka Illite - B horizon from a solonised solonetz Hundred of Laffer, South Australia.

Wyoming Bentonite - montmorillonite from Upton, Wyoming, U.S.A.

Redhill Montmorillonite - from Redhill, Surrey, England, supplied by Fullers Earth Company.

The majority of the work was carried out with these clays. However, as the work progressed it became obvious that considerable variations between minerals of the same species existed and to enable wider comparisons to be made, additional information was obtained using the following clays.

Malone Kaolinite - from Malone, Victoria, Australia, supplied by the Ceramic Section, Chemical Research Laboratories, C.S.I.R.O., Victoria, Australia.

Mercks II Kaolinite - colloidal kaolinite supplied by Mercks Chemical Company, U.S.A.

New Zealand Kaolinite - hydrothermal kaolinite, supplied by Ceramic Research Section, D.S.I.R., New Zealand.

Eureka Halloysite - from Eureka, Utah, supplied by Wards Natural Sciences Museum, U.S.A.; preheated to 110°C. to remove intra-crystalline water.

Urrbrae B Clay - B1 horizon of Urrbrae loam, a Red-brown Earth, Adelaide, South Australia; Clay content 63%. Clay fraction 60% illite, 40% kaolinite.

Panther Creek Montmorillonite - from Panther Creek, Mississippi, supplied by American Colloid Company, Chicago, Illinois, U.S.A.

Volclay Bentonite - from Wyoming, U.S.A., supplied by American Colloid Company, Chicago, Illinois, U.S.A.

Maaza Montmorillonite - from Almeria, Spain, obtained from Dr. H. Rausell-Colom, Clay Mineralogy Section, C.S.I.R.O. Division of Soils, Adelaide, South Australia.

Tidinit Montmorillonite - from North Morocco, obtained from Dr. H. Rausell-Colom, Clay Mineralogy Section, C.S.I.R.O. Division of Soils, Adelaide, South Australia.

## 2. PREPARATION OF CLAY MATERIALS.

Samples of the clays were saturated with the desired cations by repeated washing and centrifuging using in general a molar solution of the appropriate chloride. Six washes were carried out including a final overnight end over end shaking in the centrifuge bottles. Excess salt was removed by washing the materials with distilled water until they commenced to disperse or the chloride concentration in the supernatant was less than $10^{-3}$N. Volclay Bentonite and Tidinit montmorillonites were not self-dispersing when sodium saturated and were therefore rewashed with the molar salt including $10^{-3}$N hydrochloric acid to remove any unexchanged aluminium. On washing with distilled water these clays (when sodium saturated) were then found to disperse readily. Salt free samples of the clays were obtained by dialysing for two weeks using "Visking" cellulose casing.

A rough decantation process was carried out to remove the coarse sand fraction and the remainder filtered on a Buchner funnel using a Whatman Number 50 filter paper; the clay was then allowed to air dry. Violent dispersion techniques were specifically avoided to prevent the possible disruption of any natural clay structures which might exist, particularly for the divalent clays.

The clays were then gently ground to a powder and placed in a desiccator over a saturated solution of potassium sulphate giving a relative vapour pressure of 0.96 at 20°C, evacuated and allowed to equilibrate. Samples (200 and 400 mg.) of the homoionic clays were placed in the stainless steel mould (Figure 4) and compressed to 1200 atmospheres pressure by means of an hydraulic jack (Figure 5). The

FIGURE 4.

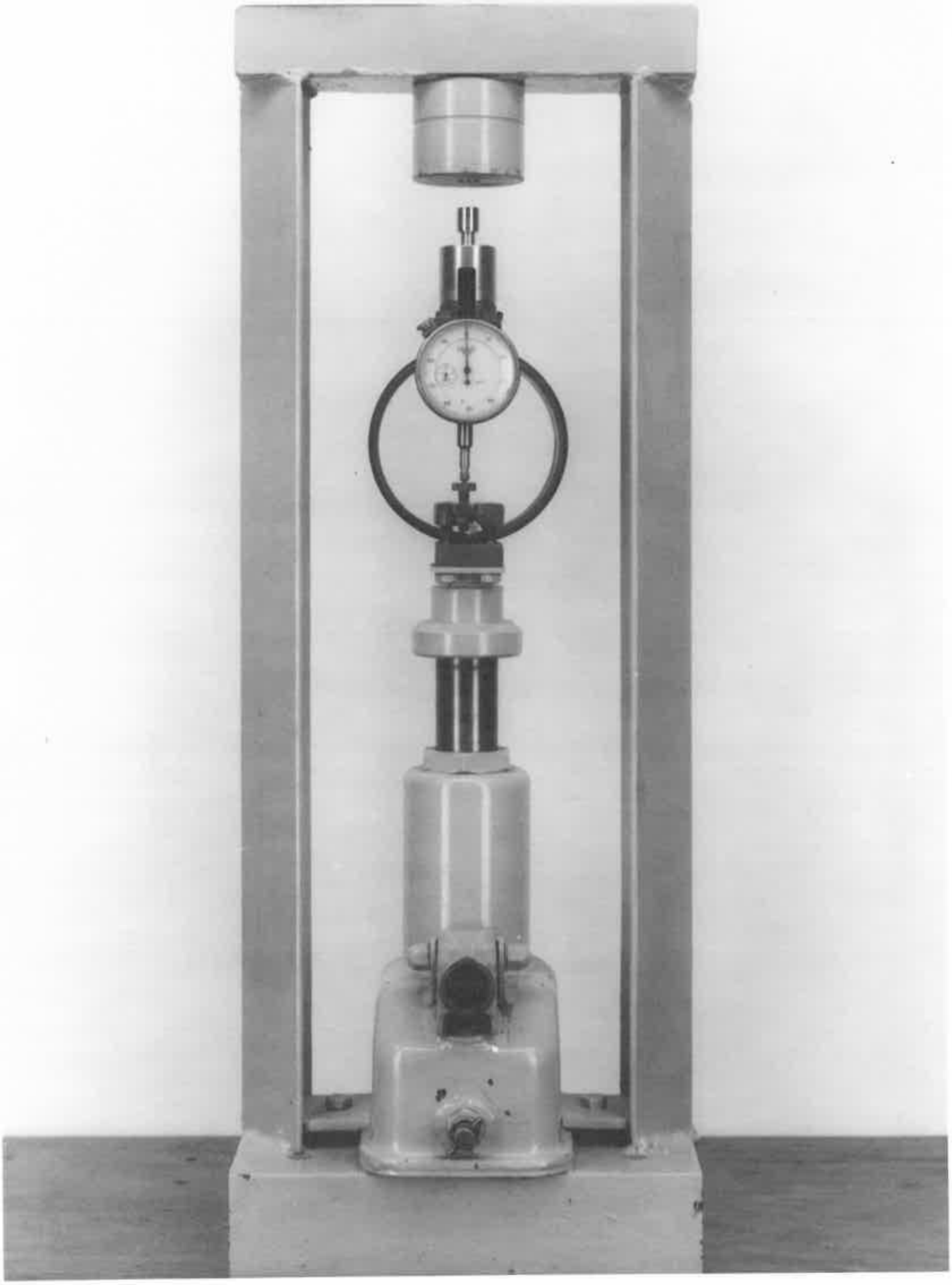


FIGURE 5.

water contents of the illite and montmorillonite powders in equilibrium with 0.96 relative vapour pressure were sufficient to give saturation under compression and hence maximum compaction. The water contents of the kaolin powders on wetting to 0.96 relative vapour pressure were not however sufficient to give saturation during the compression into cores resulting in less uniformity of packing. Increasing the water content by spraying with an atomizer to give saturation on compression, reduced the strength of the cores and made it virtually impossible to remove them from the mould and for this reason the powders in equilibrium with 0.96 relative vapour pressure were used. Although this procedure resulted in a slightly greater variation between cores for the kaolin minerals the interpretation of the results obtained is unaffected.

The small clay cores produced in this manner provided a very convenient medium for the required experimental determinations.

## 3. DETERMINATION OF EXCHANGE CAPACITIES.

Samples of the clays as previously prepared were saturated with strontium by washing with a neutral solution of molar strontium bromide. Excess salt was removed by washing with distilled water and the clays allowed to air dry. The exchange capacities were obtained as the difference between the strontium and bromine contents determined using an X-ray spectrographic method. In all samples the bromine contents were very low.

The X-ray determinations were carried out by Dr. K. Norrish, Clay Mineralogy Section, C.S.I.R.O. Division of Soils, Adelaide. The exchange capacities in milliequivalents per 100 grams of oven dry clay are given in Table 1.

TABLE 1

EXCHANGE CAPACITIES OF CLAY MINERALS.

| Clay | Exchange Capacity me/100g. | Clay | Exchange Capacity me/100g. |
|---|---|---|---|
| $Na^+$ Rocky Gully Kaolinite | 4.0 | Malone Kaolinite | 4.3 |
| $Ca^{++}$ Rocky Gully Kaolinite | 6.2 | Mercks II Kaolinite | 2.1 |
| Mercks I Kaolinite | 7.0 | New Zealand Kaolinite | 3.3 |
| $Na^+$ Grundite Illite | 24.0 | Eureka Halloysite | 7.7 |
| $Ca^{++}$ Grundite Illite | 28.2 | Maaza Montmorillonite | 120 |
| $Na^+$ Willalooka Illite | 39.1 | $Na^+$ Panther Creek Montmorillonite | 84.1 |
| $Ca^{++}$ Willalooka Illite | 41.4 | $Ca^{++}$ Panther Creek Montmorillonite | 77.3 |
| $Na^+$ Wyoming Bentonite | 92.4 | Tidinit Montmorillonite | 84.0 |
| $Ca^{++}$ Wyoming Bentonite | 101 | Volclay Bentonite | 96.2 |
| $Na^+$ Redhill Montmorillonite | 99.7 | Urrbrae B Clay | 27.6 |
| $Ca^{++}$ Redhill Montmorillonite | 93.1 | | |

## 4. SPECIFIC GRAVITY AND POROSITY DETERMINATIONS.

Specific gravities of the six principal clays were determined on the oven dried material by the volume displacement method using kerosene and 25 ml pycnometers. The apparent density of the oven dried clay cores after one wetting and drying loop were determined from the oven dried mass and overall volume of the clay cores. The porosities of the oven dried cores can then be obtained either from the relationship

$$\text{Porosity} = \frac{d_R - d_A}{d_R \times d_A} \times 100 \quad \text{cc/100g.}$$

where $d_R$ and $d_A$ are the real and apparent densities respectively, or from the difference between real and apparent volumes of the dry cores.

For the additional clays a specific gravity of 2.62 gm/cc was assumed and hence the porosities calculated for these clays can only be regarded as satisfactory estimates.

The specific gravities, apparent densities and calculated porosities of the clay cores are given in Table 2. The variation of porosity with exchangeable cation was insignificant for the six principal clays used with the exception of Wyoming Bentonite for which lower values of porosity were obtained for the monovalent than for the divalent cores. This point is discussed later.

The methods of core volume measurement are described in Section 4.

TABLE 2

SPECIFIC GRAVITIES, APPARENT DENSITIES AND POROSITIES OF CLAY CORES.

| Clay | Specific Gravity gm/cc | Apparent Density gm/cc | Porosity cc/100g. |
|---|---|---|---|
| Rocky Gully Kaolin | 2.59 | 1.75 | 18.5 |
| Mercks I Kaolin | 2.61 | 1.75 | 18.8 |
| Malone Kaolin | 2.62* | 1.75 | 18.9 |
| Mercks II Kaolin | 2.62* | 1.73 | 19.6 |
| New Zealand Kaolin | 2.62* | 1.56 | 25.9 |
| Eureka Halloysite | 2.62* | 1.75 | 18.9 |
| Grundite Illite | 2.71 | 2.04 | 12.1 |
| Willalooka Illite | 2.65 | 1.77 | 18.8 |
| Urrbrae Clay B Horizon | 2.72 | 2.00 | 13.1 |
| Wyoming Bentonite | 2.59 ($Na^+$, $K^+$.<br>($Ca^{++}$, $Mg^{++}$. | 2.04<br>1.92 | 10.4<br>13.5 |
| Redhill Montmorillonite | 2.58 | 1.85 | 15.2 |
| Maaza Montmorillonite | 2.62* | 1.90 | 14.4 |
| Panther Creek Montmorillonite | 2.62* | 1.93 | 13.6 |
| Tidinit Montmorillonite | 2.62* | 1.77 | 18.3 |
| Volclay Bentonite | 2.62* | 1.95 | 13.1 |

* Assumed.

## 5. DETERMINATION OF SPECIFIC SURFACE AREAS AND PORE SIZE DISTRIBUTION OF THE CLAY CORES.

In the determination of the surface areas of finely divided materials the B.E.T. method using low temperature van der Waals adsorption of non polar gases such as nitrogen has been universally accepted as the most reliable. Among the earliest studies using this method to determine the surface areas of soils and soil colloids were those of Emmett, Brunauer and Love (1938) using nitrogen at -183°C; Makower, Shaw and Alexander (1938) using nitrogen at -183°C and Nelson and Hendricks (1943) using nitrogen at -195°C and ethane at -78°C. Other workers to utilise this method in the study of clay minerals were Mooney, Keenan and Wood (1951, 1952), Barrer and McLeod (1954, 1955) and Birrel and Packard (1958).

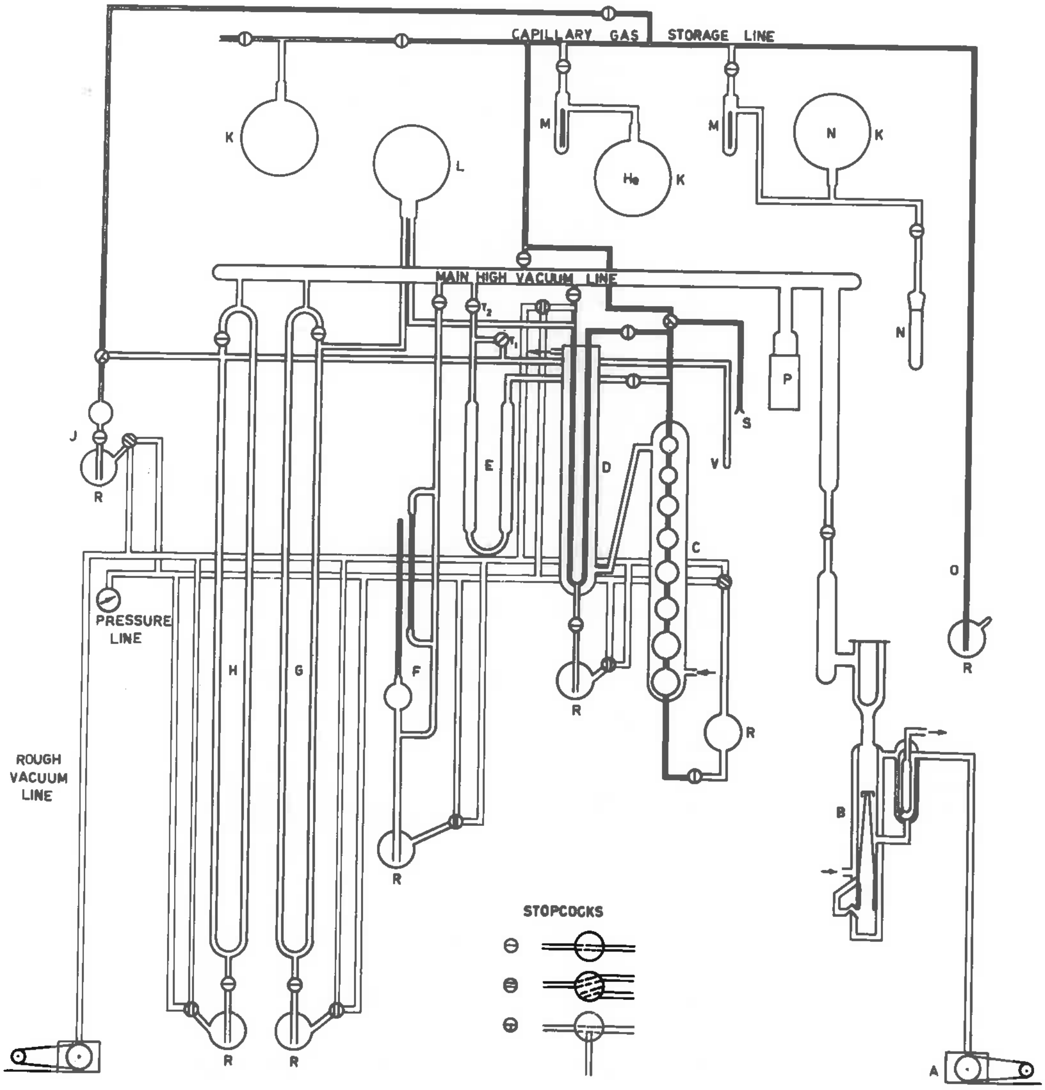
Recently Brooks (1955) has made a detailed study of the effect of dehydration at various temperatures between 25°C and 1000°C on the nitrogen sorption isotherms and surface areas determined by the B.E.T. method for several clay minerals. For such clays as kaolinite and pyrophyllite which are characterized by small cation exchange capacity and comparatively large particle size the nitrogen surface area showed little dependence on the water content of the clay until lattice destruction commenced at temperatures in the vicinity of 800°C. An illite clay showed a consistent variation of the nitrogen surface area with water content in the initial stages of dehydration at outgassing temperatures below 100°C but the surface area remained essentially constant thereafter until lattice destruction commenced at about 600°C. The montmorillonite clay (Wyoming Bentonite) not only showed considerable variation in nitrogen surface area with water content but also a marked dependence of nitrogen adsorption on the nature of the exchangeable cation, whether sodium or calcium. When sodium was the exchangeable cation the surface area consistently increased as the water content decreased until the maximum was attained at the point where only the water of constitution remained. For the calcium montmorillonite the surface area as a function of water content in the initial stages of dehydration was difficult to reproduce even when the outgassing conditions were carefully duplicated. Outgassing at 300°C produced the most reproducible surface areas without appearing to cause any loss of water of constitution and consequently this temperature was chosen for outgassing in the following determinations.

### 5.1 Apparatus.

The volumetric apparatus, a line diagram and actual photograph of which are shown in Figures 6 and 7 was built to obtain nitrogen sorption isotherms. The apparatus is similar to that of Culver and Heath (1954) which in turn was based on the original apparatus of Emmett and Brunauer (1934) and incorporated many of the refinements suggested by Harkins and Jura (1944) and Joyner (1949). The essential features of the apparatus are the sample bulb attached at S containing the clay adsorbent, a gas burette, a low pressure manometer and a high pressure manometer with mercury cut-off. The gas burette and mercury cut-off

# KEY TO FIGURE 6.

| | |
|---|---|
| A. | Rotary Vacuum Pump |
| B. | Mercury Diffusion Pump |
| C. | Gas Burette |
| D. | Mercury Cut-Off |
| E. | Low Pressure Manometer |
| F. | McLeod Gauge |
| G. | High Pressure Manometer |
| H. | Saturation Vapour Pressure Manometer |
| J. | Compression Chamber |
| K. | Gas Reservoirs |
| L. | Surge Chamber |
| M. | Rough Manometers |
| N. | Sodium Azide Decomposition Tube |
| O. | Rough Manometer |
| P. | Pirani Gauge Head |
| R. | Mercury Reservoirs |
| S. | Sample Bulb Connection Cone |
| V. | Vapour Pressure Thermometer Bulb |

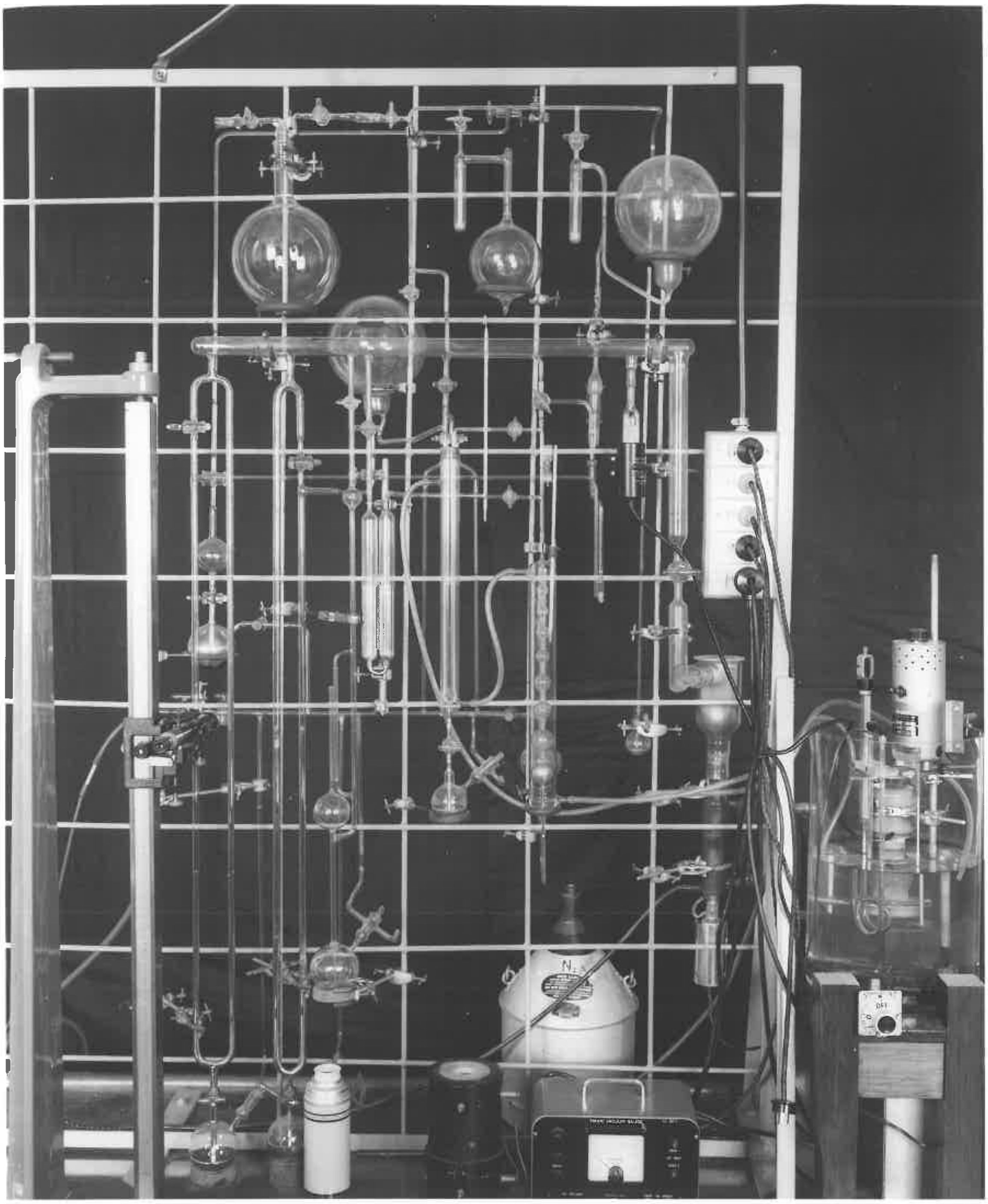


VOLUMETRIC ADSORPTION APPARATUS

FIGURE 6.

FIGURE 7

VOLUMETRIC ADSORPTION APPARATUS


N2
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are enclosed in jackets through which water from a constant temperature water bath at 25°C is pumped. The apparatus was constructed of Pyrex glass supported on a steel frame and high vacuum stopcocks greased with Apiezon N were used throughout. The vacuum was obtained by means of a two stage glass mercury diffusion pump backed by a single stage air ballasted rotary oil pump (Edwards "Speedivac" ISC30). Diffusion of mercury from the diffusion pump into the apparatus was prevented by means of the liquid air trap.

The vacuum in the main high vacuum line was measured by means of a Pirani gauge down to pressures of $10^{-3}$ mm and by a McLeod gauge for lower pressures.

A small portable furnace consisting of a 1½" diameter silica tube wound with nicrome wire and enclosed in an insulating container was used to heat the samples during the outgassing period. Furnace temperatures were controlled by a "Sunvic" energy regulator.

Sample bulbs were made from short lengths of 9 mm. glass tubing sealed at one end and drawn down after filling to join to a 6" length of 2 mm. diameter capillary tubing. The sample bulbs were attached to the apparatus by means of a standard ground glass tapered joint.

The liquid oxygen or nitrogen bath was contained in a one pint "Thermos" flask.

## 5.2 Volume Definition.

### 5.2.1 Free Space Volume.

This is the volume bounded by the top reference mark of the gas burette, the three way tap, the level of the mercury in either manometer E or cut off D depending on which manometer is in use. The free space was calibrated indirectly from pressure-volume relations (see Appendix 1.1.2) using the gas burette and since it is subject to fluctuations in room temperature was kept as small as possible by using 2 mm. capillary tubing. Variations in free space temperature were kept to a minimum by the installation of a Chrysler "Airtemp" room conditioner.

### 5.2.2. Dead Space Volume.

This is the volume of the sample bulb and connecting tube to the three way tap excluding the volume occupied by the sample. The volume of the dead space at the temperature of the free space is much smaller than that at the temperature of the liquid nitrogen (oxygen) bath and can be neglected. The dead space is determined from volume and pressure changes using helium which is assumed to be unadsorbed at liquid nitrogen (oxygen) temperatures (see Appendix 1.1.3).

## 5.3. Pressure Measurement.

### 5.3.1. Low Pressure Range.

Gas pressures up to 100 mm. in the adsorption system were measured by the low pressure mercury manometer. This manometer was constructed of 25 mm. internal diameter precision bore tubing and the mercury levels were read by means of a cathetometer reading to 0.01 mm. by Vernier. Due to the large diameter of the tubing and its uniformity, errors due to capillary effects are negligible. The volume increment in the free space can be calculated readily from the known factor for the volume per unit length of the precision bore tubing (see Appendix 1.1.2).

### 5.3.2. High Pressure Range.

Since it is impractical to use precision bore tubing to reduce capillary effects, the high pressure manometer was constructed of standard 10 mm. tubing enabling manometer readings accurage to 0.1 mm. to be obtained. The interposition of a mercury cut-off (Emmett and Brunauer, 1934; Harkins and Jura, 1944) of 2 mm. diameter between the adsorption system and the high pressure manometer, removes the necessity to bring the mercury level in the short arm of the manometer to a fixed reference mark and reduces the volume variation in the free space due to inaccurate settings of the mercury level to less than 0.001 $cm^3$. The adjustment of the mercury levels in the cut-off is facilitated by the inclusion of a three litre surge chamber between the manometer and the cut-off. Free space calibration for this manometer is given in Appendix 1.1.2.

### 5.4 Gases.

"Spectrally pure" helium was obtained in 1 litre Pyrex flasks from the British Oxygen Company. These flasks were sealed onto the apparatus, evacuated and opened in the usual way with a magnet and iron rod.

Pure nitrogen was prepared by the thermal decomposition of A.R. sodium azide. (Honig and Reyerson, 1952). Sufficient sodium azide to give three litres of nitrogen at S.T.P. was placed in the tube, evacuated for twelve hours at a temperature of 200°C and then thermally decomposed at 300°C in vacuo.

## 5.5 Determination of Saturation Vapour Pressure ($p_o$).

The saturation vapour pressure was measured by means of the vapour pressure thermometer when liquid nitrogen was used in the bath in the determination of complete adsorption-desorption isotherms. Commercial liquid nitrogen was found unsatisfactory for use as a bath as it gave a saturation vapour pressure in excess of 900 mm. A purer liquid was obtained by passing cylinder nitrogen at 200 lbs/sq.in. into a copper spiral immersed in the impure liquid nitrogen. This provided a saturation vapour pressure very close to 760 mm.

Liquid oxygen was used as a bath for some of the surface area determinations and for these the saturation vapour pressure was assumed to be that at the boiling point of the liquid oxygen. Where surface area determinations were made by both methods on the same sample agreement was excellent.

The left arm of the low pressure manometer is connected by a tap to the vapour pressure thermometer bulb so that it can be used to register ($p_o$ - p) directly and relative pressures approaching unity can be measured accurately. This is achieved by opening tap $T_1$ shown in Figure 6 and closing tap $T_2$ to the main vacuum line.

## 5.6 Procedure.

The clay cores were placed in the sample bulb, connected to the apparatus and outgassed at a temperature of 300°C for 25 hours or until the pressure remained below $10^{-3}$ mm. after isolation from the pumps for half an hour. The sample bulb was then immersed in the liquid nitrogen or oxygen bath and the dead space determined using helium gas. The system was re-evacuated and the isotherm obtained essentially in the manner described by Emmett (1942) by measuring successive quantities of nitrogen into the gas burette-free space system and then opening to the sample at the temperature of the bath. At equilibrium the appropriate pressure and temperature measurements were made and the volume of gas adsorbed at .S.T.P. calculated as shown in Appendix 1.2. Equilibrium was found to occur fairly rapidly (5-10 mins.) for relative pressures below 0.5, increasing to about 20 mins. for points near saturation.

## 5.7. Results and Discussion.

Surface areas of the clay materials, obtained by application of the B.E.T. theory to nitrogen adsorption isotherms, are given in Table 3. The B.E.T. plots for these are reproduced in Appendix 1.3. For the clays for which the sand decantation could produce significant variations, surface areas were determined on both monovalent and divalent samples. For the remainder the surface areas were determined on the calcium clays. The larger surface area of the calcium Grundite illite compared with the sodium Grundite illite can therefore be ascribed to a more efficient sand decantation in the calcium case. The progressive increase in surface area of the Wyoming Bentonite from the natural to the calcium to the sodium clay, does however seem to indicate a genuine decrease in average particles size with consequent increase in surface area since the initial sand content being less than 10 per cent could not account for this change. This variation is later considered in more detail.

To examine the micro-structure of the clay cores used in the swelling work complete nitrogen adsorption-desorption isotherms were obtained for cores of the six principal clays. The isotherms for the calcium cores are shown in Figures 8 to 13. To illustrate the distribution of pores within the cores differential plots of the volume adsorbed per gram with respect to relative vapour pressure against relative vapour pressure i.e. $\frac{dV}{d(p/p_o)}$ against $p/p_o$, are given in Figures 14 to 19. The equivalent cylindrical pore radii calculated on the basis of the Kelvin equation are indicated on the bottom ordinate. The linear $(p/p_o)$ scale was considered more convenient for the purpose of illustration than a true pore size distribution plot of $\frac{dV}{dr}$ against r, since the latter involves the inverse logarithmic relationship between $p/p_o$ and r and provides little further information.

The interpretation of equivalent pore radii calculated on the basis of the Kelvin equation must be made with some caution. The vapour pressure lowering over a curved meniscus is calculated as a function of $(\frac{1}{r_1} + \frac{1}{r_2})$ where $r_1$ and $r_2$ are the principal radii of curvature of the meniscus. It is assumed that the meniscus has a hemispherical shape on desorption and the vapour pressure lowering is then a function of $(\frac{1}{r_1} + \frac{1}{r_1}) = \frac{2}{r_1}$. However in the case of pores existing between large

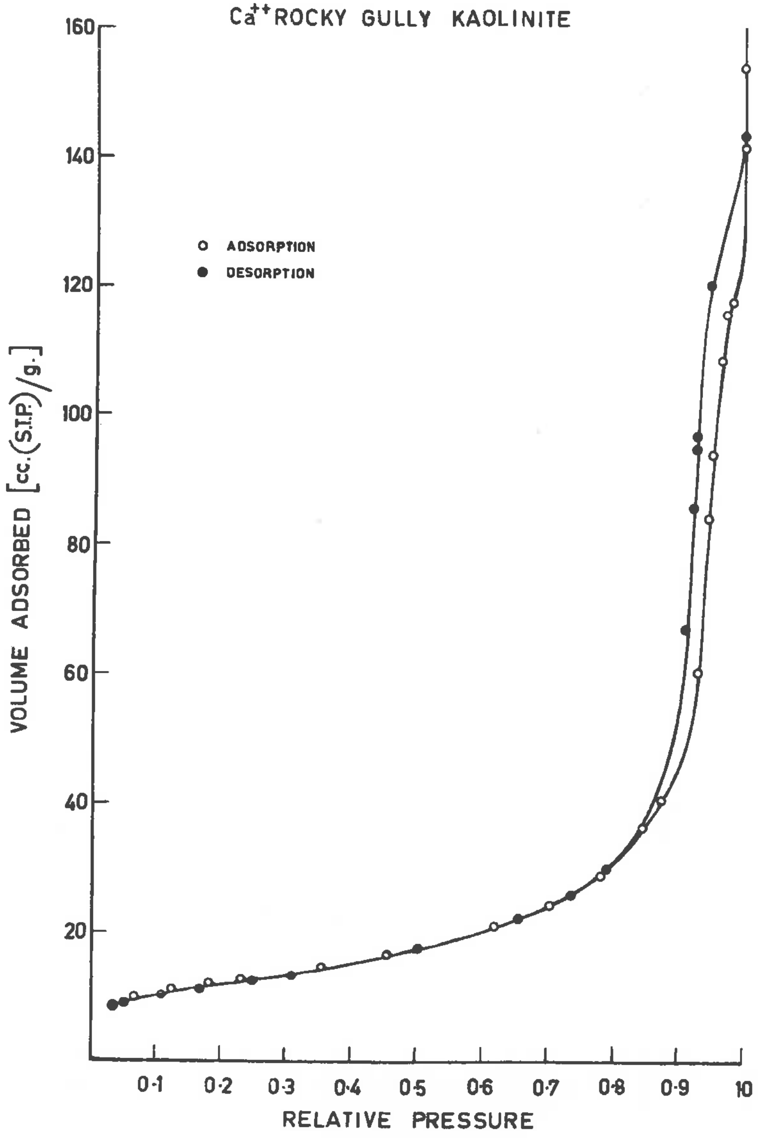


FIGURE 8.

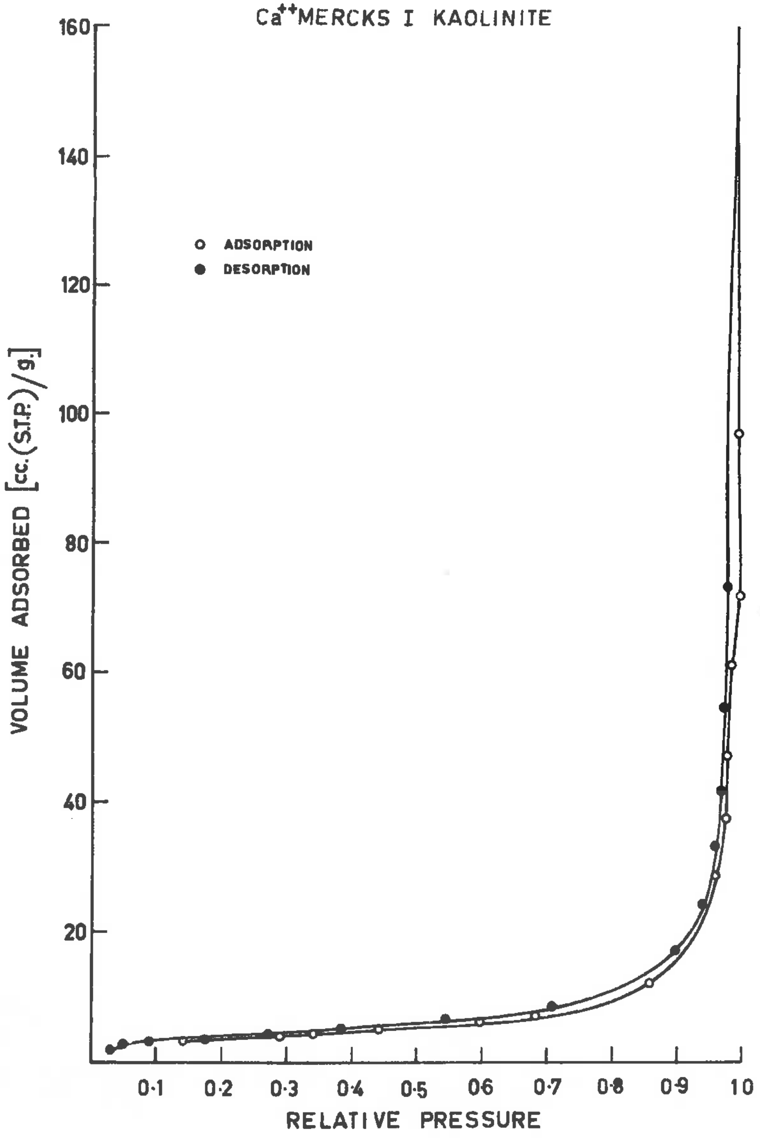


FIGURE 9.

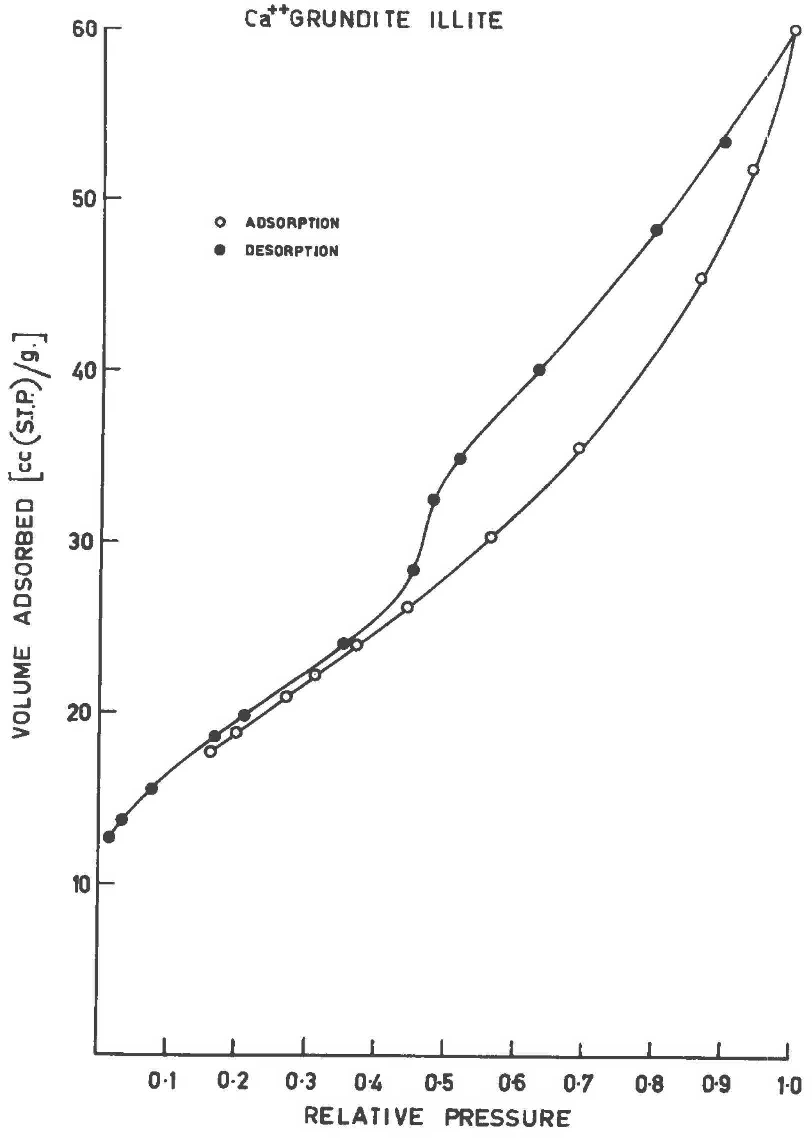


FIGURE 10.

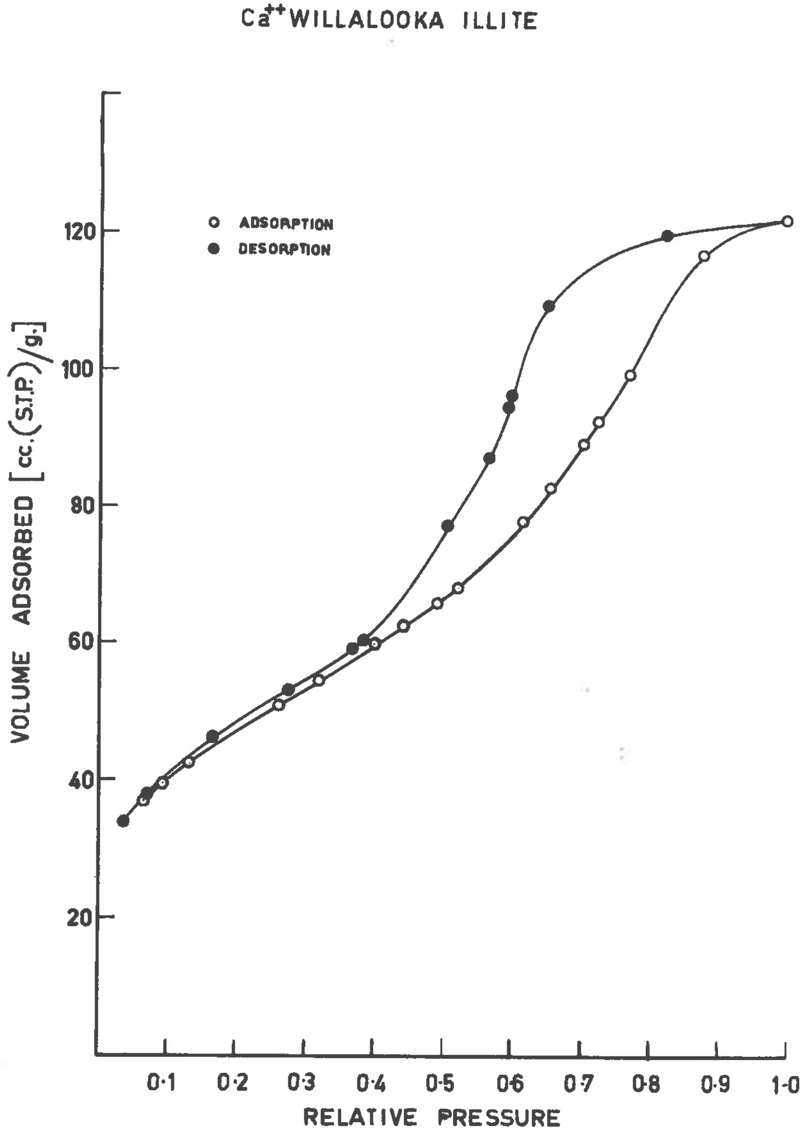


FIGURE 11.

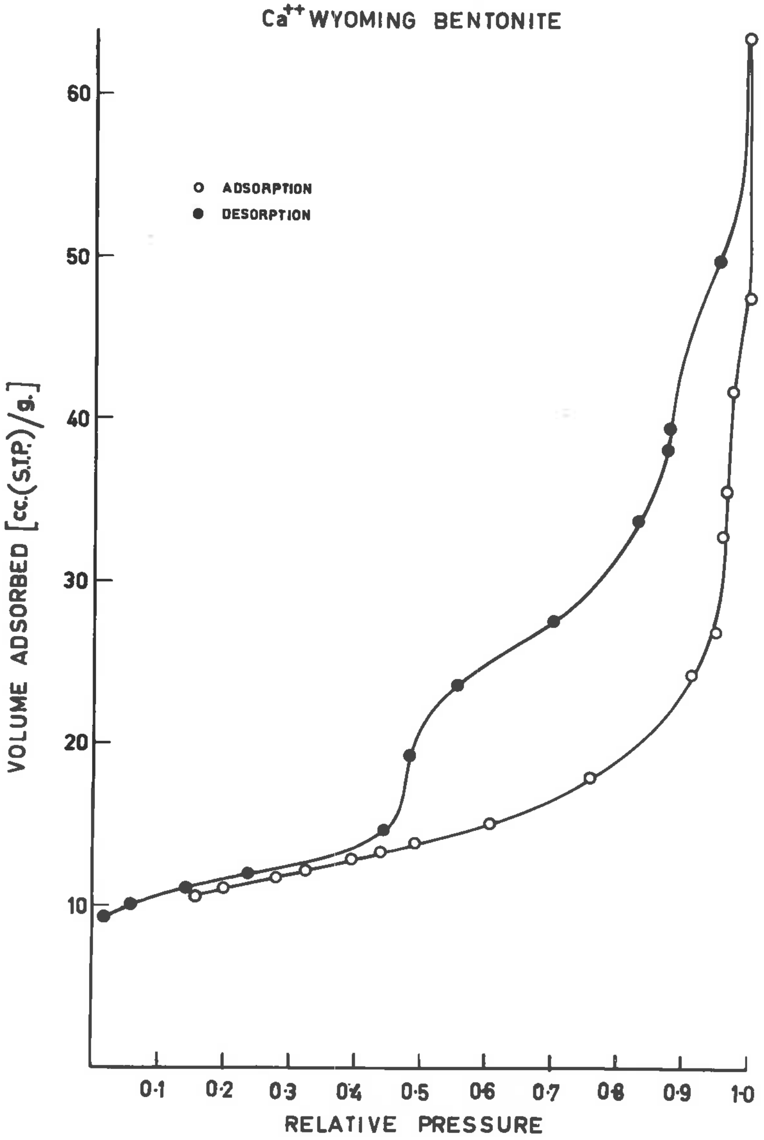


FIGURE 12.

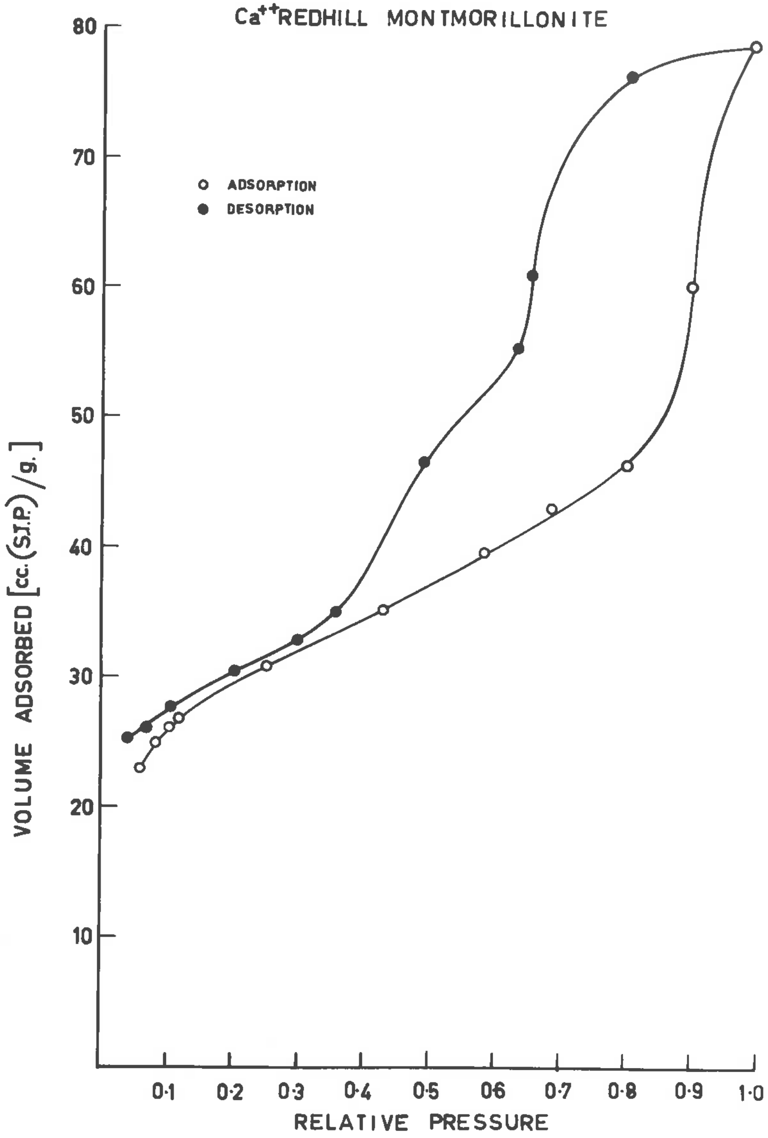


FIGURE 13.

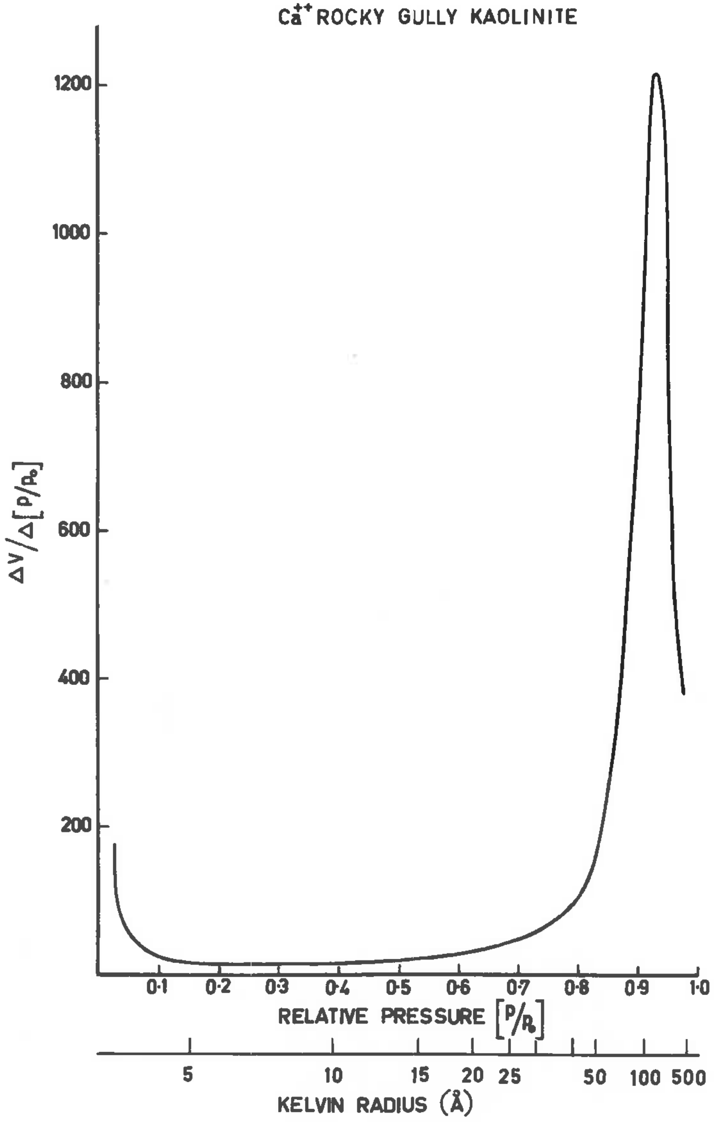


FIGURE 14.

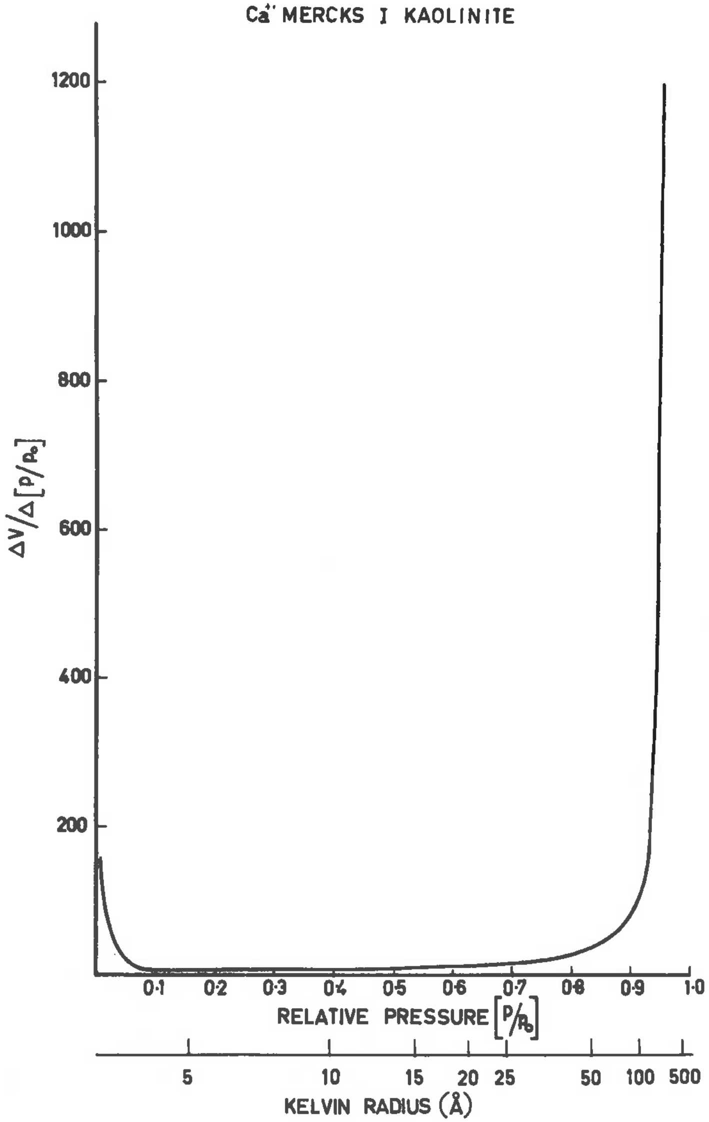


FIGURE 15.

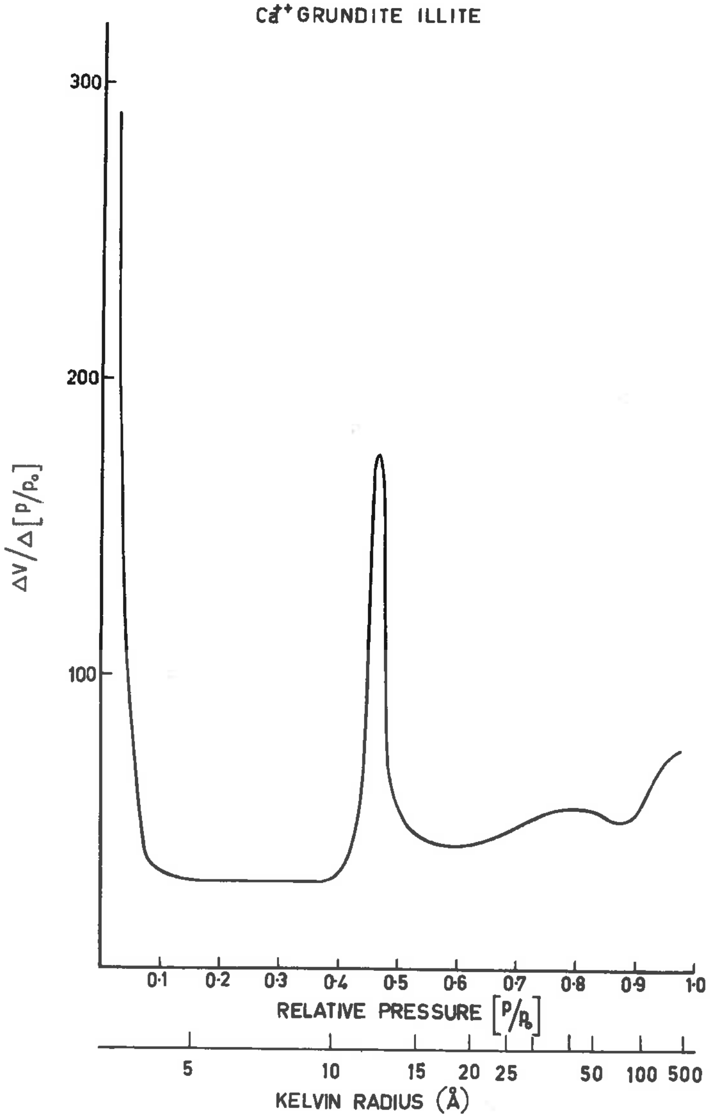


FIGURE 16.

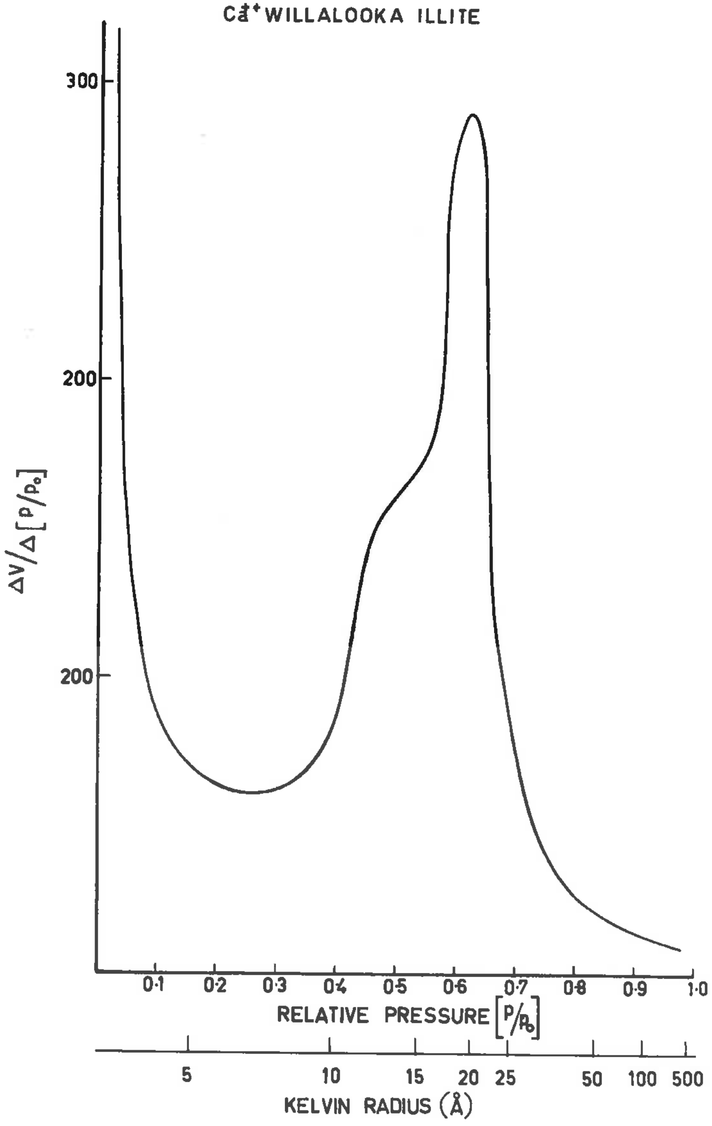


FIGURE 17.

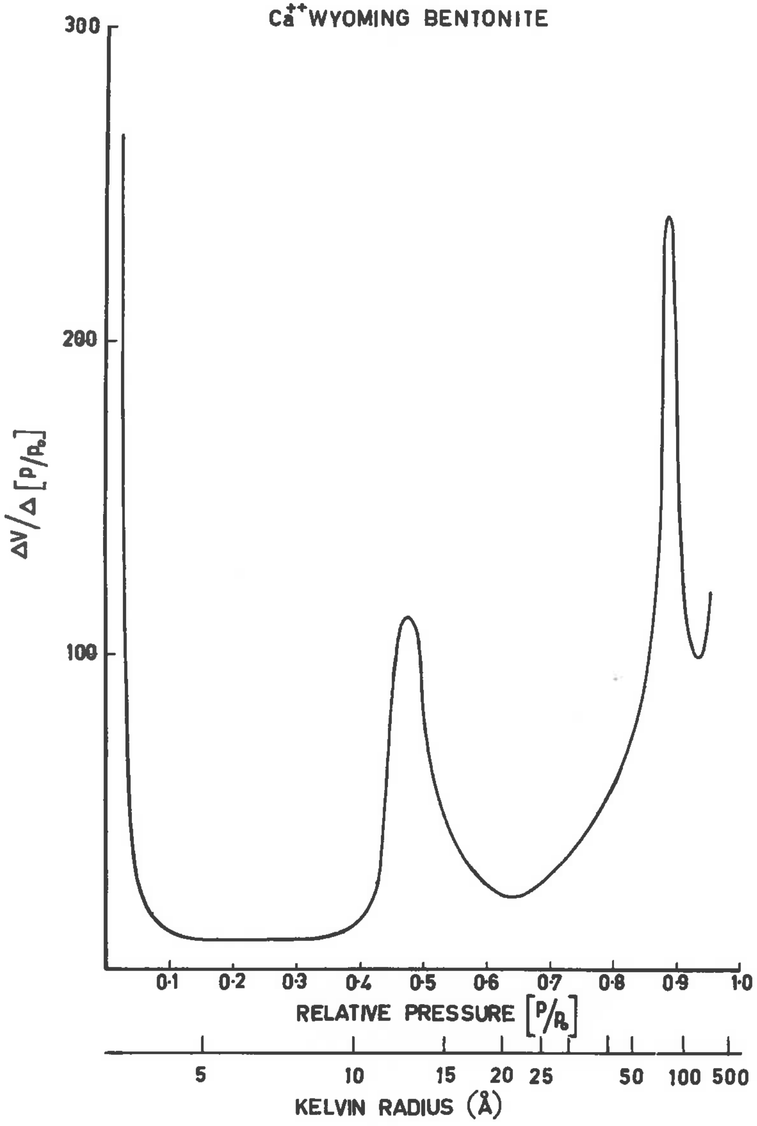


FIGURE 18.

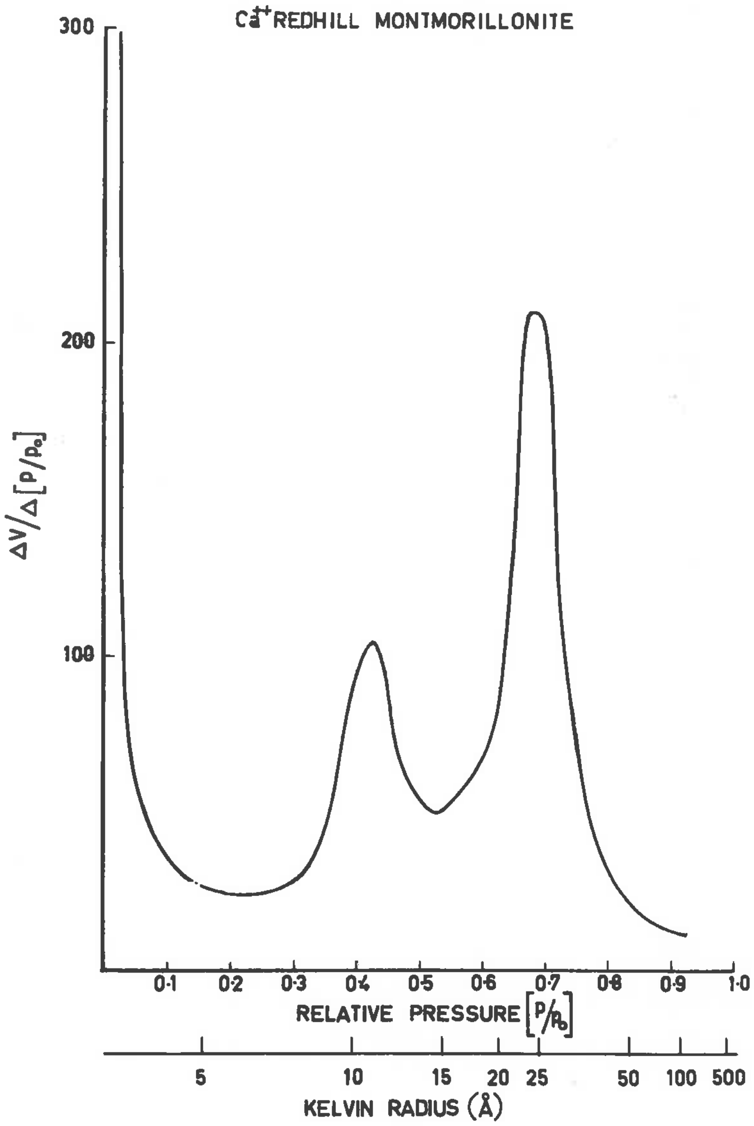


FIGURE 19.

## TABLE 3

## SPECIFIC SURFACE AREAS OF CLAY MINERALS

| Clay | Vm<br>cc S.T.P./gm. | Specific Surface Area<br>m2/gm. |
|---|---|---|
| $Ca^{++}$ Rocky Gully Kaolinite | 8.33 | 36.3 |
| $Ca^{++}$ Mercks I Kaolinite | 2.64 | 11.5 |
| $Ca^{++}$ Mercks II Kaolinite | 2.58 | 11.2 |
| $Ca^{++}$ Eureka Halloysite | 25.21 | 109.8 |
| $Ca^{++}$ N.Z. Kaolinite | 9.24 | 40.2 |
| $Ca^{++}$ Malone Kaolinite | 3.99 | 17.4 |
| $Na^{+}$ Grundite Illite | 12.55 | 54.7 |
| $Ca^{++}$ Grundite Illite | 14.73 | 64.2 |
| $Na^{+}$ Willalooka Illite | 34.45 | 150.1 |
| $Ca^{++}$ Willalooka Illite | 35.18 | 153.3 |
| Natural Wyoming Bentonite | 5.32 | 23.2 |
| $Na^{+}$ Wyoming Bentonite | 11.06 | 48.2 |
| $K^{+}$ Wyoming Bentonite | 10.83 | 47.2 |
| $Ca^{++}$ Wyoming Bentonite | 8.74 | 38.1 |
| $Na^{+} \rightarrow Ca^{++}$ Wyoming Bentonite | 8.78 | 38.3 |
| $Na^{+}$ Redhill Montmorillonite | 23.81 | 103.8 |
| $Ca^{++}$ Redhill Montmorillonite | 22.82 | 99.4 |
| $Ca^{++}$ Maaza Montmorillonite | 15.28 | 66.6 |
| $Ca^{++}$ Panther Creek Montmorillonite | 15.83 | 68.9 |
| $Ca^{++}$ Tidinit Montmorillonite | 21.39 | 93.2 |
| $Ca^{++}$ Volclay Bentonite | 7.47 | 32.5 |
| Urrbrae B Clay Natural Aggregates | 21.53 | 93.8 |
| $Ca^{++}$ Urrbrae B Clay | 20.83 | 90.7 |

parallel or near parallel opposed plates the shape of the meniscus on desorption would be cylindrical and $r_2$ would approximate to infinity. The vapour pressure lowering would then be a function of $\left(\frac{1}{r_1} + \frac{1}{\infty}\right) = \frac{1}{r_1}$. Since it seems probable that a considerable proportion of the porosity of a mass of compacted plate shaped particles would arise in this fasion, the equivalent cylindrical radii calculated on the basis of the Kelvin equation could possibly be better regarded as estimates of average plate separations at least for pores small in comparison with plate dimensions (say < 100 Å). If Foster's (1932) suggestion is correct this estimate should be increased by twice the thickness of an adsorbed monolayer (approx. 8 Å).

The isotherms for the two kaolins are characteristic for materials of relatively coarse particle size and are of type II of Brunauer's classification. Both isotherms show little hysteresis and the majority of the porosity contained in relatively large pores. For Rocky Gully kaolinite, after the initial monolayer uptake the differential plot remains flat until a relative pressure of 0.7 and then rises to a peak at approximately 0.93 corresponding to an equivalent cylindrical pore radius of 130 Å. For Mercks I kaolinite the majority of the desorption takes place at equivalent cylindrical pore radii in excess of 200 Å. This is consistent with the larger particle size of the Mercks kaolinite as indicated by the smaller specific surface area. It is conceivable that with the relatively large crystals encountered in kaolinites, equivalent cylindrical pore radii or rather surface separations up to the order of 100 Å could easily arise from steps in the crystal surfaces between parallel crystals as well as from separations between neighbouring crystals.

The isotherms for the illite and montmorillonite cores have a number of interesting features in common. All are characterized by appreciable hysteresis above 0.4 relative pressure followed by a small but persistent hysteresis down to very low relative pressures. Similar hysteresis effects in nitrogen isotherms on finely divided material have been noted by several other workers. Brooks (1955) explained the presence of hysteresis at low relative pressures ($< 0.4$) in the nitrogen sorption isotherms for calcium montmorillonite as being due to the propping apart of interlamellar spacings by residual water molecules giving rise to a structural instability of the material. This could account for the augmented nitrogen adsorption capacity on the desorption branch of the isotherm down to very low relative pressures. The disappearance of this micropore hysteresis after the removal of most of the water of adsorption and hydration by a prolonged outgassing for 152 hours at 25°C and 4 hours at 60°C at $10^{-5}$ mm. mercury pressure, gave support to this concept. Low relative pressure hysteresis was not however evident in the isotherms obtained by Brooks for native (sodium) Wyoming Bentonite and in this case he considered that the intra crystalline spacing (2.80 Å corresponding to one water layer) was too small to allow nitrogen penetration (diameter of nitrogen molecule = 4.2 Å).

McDermot and Arnell (1955, 1956) in studying the properties of brominated graphites where the situation is not unlike that for the montmorillonites with both intercrystalline and intracrystalline sorption of bromine, have also demonstrated the existence of two types of hysteresis in nitrogen isotherms for these structures with an expanding

C axis. These workers believed the broad hysteresis loop extending from saturation down to relative pressures of approximately 0.45 to be due to the porous nature of the graphite and designated it as "pore" hysteresis. The second type of hysteresis which they termed "swelling" hysteresis was attributed to the availability of volume within the swollen graphite crystals after the removal of most of the bromine. The term intercrystalline swelling was used by these workers but the phenomenon as described is probably more aptly termed intracrystalline.

The persistence of this latter type of hysteresis in the present work on calcium Wyoming Bentonite after the stronger outgassing procedure and its presence for the illite cores and possibly Mercks I kaolinite as well, seems to indicate its origin in this case as an intercrystalline rather than an intracrystalline phenomenon. This could arise if there were any appreciable stacking of the plate-like crystals of these minerals in the drying or consolidation process. Similar conditions for a structural instability as envisaged by Brooke would then occur.

It is interesting to note that Barrer and MacLeod (1955) after creating what might be considered the ideal situation for this swelling hysteresis by the interlamellar adsorption of tetra alkyl ammonium ions, observed this swelling hysteresis in sorption isotherms of argon and methane on a $N(C_2H_5)^+$-montmorillonite at 90°K but not as 78°K. The values obtained for surface areas indicated that oxygen and nitrogen were also intercalated in the tetra alkyl ammonium montmorillonites but swelling hysteresis was not evident for these gases. The amounts of the respective gases adsorbed in the $N(C_2H_5)^+$-clay at a given relative pressure were in the order $O_2 > N_2 > A > CH_4$ which is the inverse of the molecular cross-sectional diameter indicating that size has a definite effect on the amount which can be intercalated. Temperature of adsorption was also found to be important in determining the amount of gas adsorbed, more being adsorbed at 90°K than at 78°K.

It can be seen that for both montmorillonites and the Grundite illite there is a characteristic shoulder in the desorption branch of the nitrogen isotherm at a relative pressure of about 0.45. An explanation of these shoulders has been postulated by Barrer and MacLeod (1954) who suggested the possibility of the clay particles being drawn by surface tension forces into a thixotropic structure (after lubrication by a film of capillary condensate) and that this more regular array retains capillary condensed sorbate more tenaciously on desorption than does a purely random array. When the film of capillary condensate becomes sufficiently attenuated however the suggestion is that it may fail to lubricate and hold together the thixotropic structure which would then randomize again and must in doing so give up the remaining condensate. Such behaviour would indicate a very weak attraction between individual crystals of these clays and a very strong thixotropic tendency.

On the other hand the isotherm for the Willalooka illute exhibits no such shoulder which may indicate that very strong bonding occurs between the crystals of this clay thus preventing movement by surface tension forces.

Alternatively it may be argued that little significant rearrangement of the clay particles, after the progressive removal of water, will occur in the presence of a non-polar liquid such as nitrogen. That is, the shoulders in the desorption branch of the isotherm may actually reflect the presence of a narrow range of pores of approximately 12 Å equivalent cylindrical radius (corresponding to 0.45 relative pressure). Applying the considerations discussed earlier this would correspond to plate separations of the order of 20 Å.

It is equally interesting to compare the distribution of the pores within the clay cores. In Table 4 the volumes of liquid nitrogen retained at various relative pressures on the desorption isotherm are compared with the total oven dry (110° C) porosities as previously measured.

TABLE 4

VOLUME OF LIQUID NITROGEN RETAINED AT VARIOUS RELATIVE PRESSURES.

| Relative Pressure | | 0.9 | 0.8 | 0.75 | Specific Surface Area $m^2/g$. |
|---|---|---|---|---|---|
| Equivalent Kelvin Radius (Å) | | 90 | 42 | 33 | |
| Clay | Oven Dry Porosity cc/100g. | Volume of Liquid Nitrogen retained cc/100g. | | | |
| $Ca^{++}$ Rocky Gully Kaolinite | 18.5 | 9.9 | 4.8 | 3.4 | 36.3 |
| $Ca^{++}$ Mercks I Kaolinite | 18.8 | 4.3 | 1.7 | 1.5 | 11.5 |
| $Ca^{++}$ Grundite Illite | 12.1 | 8.2 | 7.4 | 7.1 | 64.2 |
| $Ca^{++}$ Willalocka Illite | 18.8 | 18.7 | 18.6 | 18.2 | 153.3 |
| $Ca^{++}$ Wyoming Bentonite | 13.5 | 6.8 | 5.0 | 4.5 | 38.1 |
| $Ca^{++}$ Redhill Montmorillonite | 15.2 | 12.0 | 11.8 | 11.4 | 99.4 |

The volume of liquid nitrogen retained at any particular value of relative pressure is related to the particle size and specific surface area as is to be expected. However, it is interesting to note that almost the entire porosity of the Willalooka cores is accommodated in pores having equivalent cylindrical radii less than 33 Å. From the differential plot it can be seen that the peak of the pore size distribution for this clay occurs at a relative pressure of approximately 0.625 corresponding to an equivalent cylindrical pore radius of 20 Å. Since the crystal plates of this clay are probably of the order of 700 Å across the cleavage face, this equivalent cylindrical radius may be interpreted, on the addition of twice the monolayer thickness, as a separation between crystal sheets of the order of 28 Å. If the oven dry porosity of the clay is divided by the specific surface area the average half distance between crystals so calculated is 13 Å. It may therefore be inferred that the matrix of the Willalooka cores consists of the clay plates highly organized on a micro-scale into oriented packets or domains with very few large pores between domains. It is difficult to visualise such a relatively narrow band of pore sizes arising in any other fashion than this for plate shaped particles, although the reason for crystals remaining at such high separations in the dry state is not clear. The presence of surface irregularities on the clay crystals may be envisaged as holding the majority of the surfaces at appreciable separations. Alternatively the separations may be considered to arise from mutual repulsion of the surface charge distributions. In this regard the approach of one plate to another in the dry state could possibly provide a net repulsive force such as may result from the approach of a positive charge (surface cation) to a dipole (arising from the separation of the exchangeable cation on the adjacent sheet from the site of isomorphous replacement by the layer of oxygen atoms).

It may be argued of course that the crystal sheets may be very much closer within domains with a large volume of interdomainal pores of the order of 28 Å, but unless a large proportion of the surface area is not available to nitrogen adsorption this would necessitate the presence of a considerable volume of much larger pores between domains to provide the same total porosity. Considerations discussed later do however indicate that essentially the total surface area is available to nitrogen adsorption.

For the Grundite illite the nitrogen desorption isotherm and the differential plot indicate that after the initial shoulder at approximately 0.45 relative pressure, there is a continuous range of pore sizes up to several hundred angstroms and greater. This may be interpreted as indicating a less developed domain structure for this clay resulting in a greater variation in pore dimensions between domains. Alternatively if the formation of a thixotropic structure by surface tension forces as suggested by Barrer and MacLeod is correct, the range of pore sizes might simply reflect the nature of this structure since it is difficult to predict at what point on the desorption isotherm such forces would exert an influence.

For the montmorillonites the second peak on each of the differential curves (at 0.885 and 0.675 relative pressures corresponding to equivalent cylindrical radii of 77 Å and 24 Å or plate separations of

85 Å and 32 Å for Wyoming Bentonite and Redhill montmorillonite respectively) may be interpreted as arising from larger intradomainal spacings resulting from the contraction of the crystals after the formation of the clay matrix structure during the drying process. The increased separation for the Wyoming Bentonite possibly results from the larger crystal size. The first peak on each curve (indicating plate separations of approximately 20 Å in each case) may then correspond either to the areas of closest possible approach of the clay crystals in a fixed structure, in which case some mechanical hindrance or repulsive force is implied or else to a reshuffling of the clay crystals by surface tension forces as envisaged by Barrer and Macleod, followed by a relaxation as the liquid film becomes attenuated.

The isotherms and differential plots for the kaolinite clays give little indication of a similiar packing into domains but here the large crystal dimensions and possibly larger surface irregularities such as stepping may prevent the close approach of the major part of the clay surfaces to less than 50 or 100 Å. The relatively small surface areas of the kaolinites, in particular the Mercks I kaolinite, may result in comparatively insignificant volumes of liquid nitrogen being retained between the areas of closer approach (say 20 - 30 Å).

Crystal surface separations of less than 4 Å would prevent the measurement of these surfaces by nitrogen adsorption due to the dimensions of the non-polar nitrogen molecules. However, such surfaces would be accessible to polar molecules such as water. If it is assumed that a monolayer of water molecules is adsorbed on a clay surface at a relative vapour pressure of approximately 0.20 (Orchiston, 1953;

Quirk, 1955), some indication of the surface area not accessible to nitrogen adsorption may be obtained. In Table 5. the surface areas calculated from water vapour adsorption data on the sodium clays (given in Section 4) have been compared with those obtained by the nitrogen adsorption method. The sodium clays were chosen to reduce the effect of hydration of the exchangeable cations on the water vapour estimate of surface area.

TABLE 5

COMPARISON BETWEEN WATER VAPOUR AND NITROGEN SURFACE AREAS

| | Specific Surface Area | |
|---|---|---|
| Clay | Water Vapour Adsorption $m^2/g$ | Nitrogen Adsorption $m^2/g$ |
| Rocky Gully Kaolinite | 30 | 36 |
| Mercks I Kaolinite | 14 | 11.5 |
| Grundite Illite | 54.2 | 54.7 |
| Willalooka Illite | 166 | 150 |
| Wyoming Bentonite | 184 (54.2)* | 48 |
| Redhill Montmorillonite | 129 | 104 |

* Value in brackets was obtained from water content at 0.19 relative vapour pressure after clay had been oven-dried at 110°C.

The water vapour adsorption values used were those obtained in equilibrium with 0.19 relative vapour pressure after predrying by evacuation over phosphorus pentoxide powder by means of a water pump. The value in brackets for the Wyoming Bentonite was calculated from the water vapour adsorbed at 0.19 relative vapour pressure after oven drying at 110°C. In view of the probable effects of hydration of the exchangeable sodium cations the water vapour estimate of surface area can only be regarded as very approximate but should provide if anything an overestimate of the surface area. The general agreement for the kaolinite and in particular the illite clays can therefore be taken as an indication that essentially the same surface area is available for both water and nitrogen adsorption on these clays. Certainly large areas do not appear to be inaccessible to nitrogen molecules. However for the Wyoming Bentonite the discrepancy between the value obtained after apparently incomplete drying over phosphorus pentoxide and the nitrogen surface area can be ascribed to the greater availability of intracrystalline surfaces to water molecules in the former case. It is apparent that this availability is considerably less after oven drying at 110°C. Oven drying appears to be capable of removing almost all the interlamellar water from the sodium clay resulting in the collapse of most intracrystalline spacings. On rewetting to 0.19 relative vapour pressure the surface area obtained showsbetter agreement with the nitrogen surface area. The remaining clays including Redhill montmorillonite showed little variation in water content at 0.19 relative pressure between the two predrying procedures.

These considerations appear to support the concept of the crystal sheets being held at appreciable separations and being only in contact at very few points.

An additional check on the distances of approach of crystal surfaces may be made by calculating the equivalent pore radius at which the surface area of the vapour-liquid interface created by desorption is equal to that calculated by the B.E.T. method. The area of a vapour-liquid interface created by desorption in a capillary (Payne, 1953) is given by

$$S = \frac{1}{\gamma}\int p \, dv$$

where S is the area of the liquid surface, v is the volume of liquid retained at pressure p and $\gamma$ its surface tension. By plotting v, the volume in cc of liquid nitrogen retained against the applied suction in dynes/cm$^2$ i.e. $\frac{RT}{V} \ln {}^{p}/_{p_o}$ the value of $\int p \, dv$ at any particular value of p can be obtained from the area enclosed by the curve and the value of the ordinate v. The value of relative pressure and hence equivalent cylindrical pore radius at which the surface area calculated by this method is equal to the B.E.T. surface area can then be obtained from the nitrogen isotherm. The minimum values of equivalent cylindrical radii and hence by the addition of two monolayers thickness the equivalent plate separations within which the total surface areas of the clays are contained are shown in Table 6.

TABLE 6

| Clay | Rocky Gully Kaolin | Marcks I Kaolin | Grundite Illite | Willalooka Illite | Wyoming Bentonite | Redhill Montmorillonite |
|---|---|---|---|---|---|---|
| Equivalent Cylindrical Radius (Å) | 28 | 39 | 7.9 | 6.5 | 11.8 | 5.7 |
| Separation Between Plates (Å) | 36 | 47 | 16 | 15 | 20 | 14 |

This method is again only approximate but nevertheless can be taken as additional evidence that the clay surfaces are for the major part held at appreciable separations since the entire surface area appears to be accommodated in pores equivalent to separations greater than 14 Å.

The progressive increase in specific surface area from the natural to the calcium to the sodium Wyoming Bentonite could be interpreted as arising from the loss of one or two lamellæ from individual crystals whilst in suspension. Alternatively it may indicate that the monovalent clay is dispersed into unit lamellæ in suspension and that a stronger statistical reformation of crystals occurs for the calcium clay on drying than for the sodium clay. This latter concept is strongly supported by the fact that a sample of the sodium saturated clay on dispersing in distilled water and then calcium saturating with molar calcium chloride, on washing and drying, has an almost identical surface area as the original calcium clay. In Figures 20 and 21 the nitrogen isotherms for the sodium and sodium —> calcium Wyoming Bentonite clays respectively are shown. The sodium clay obviously has a greater number of pores

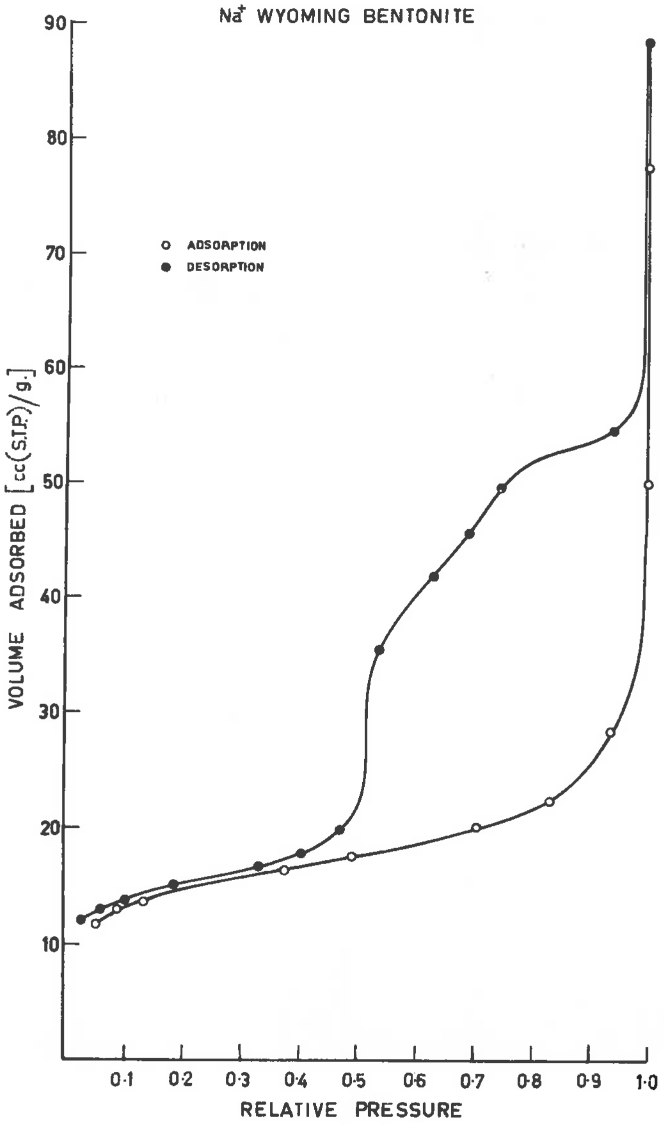


FIGURE 20.

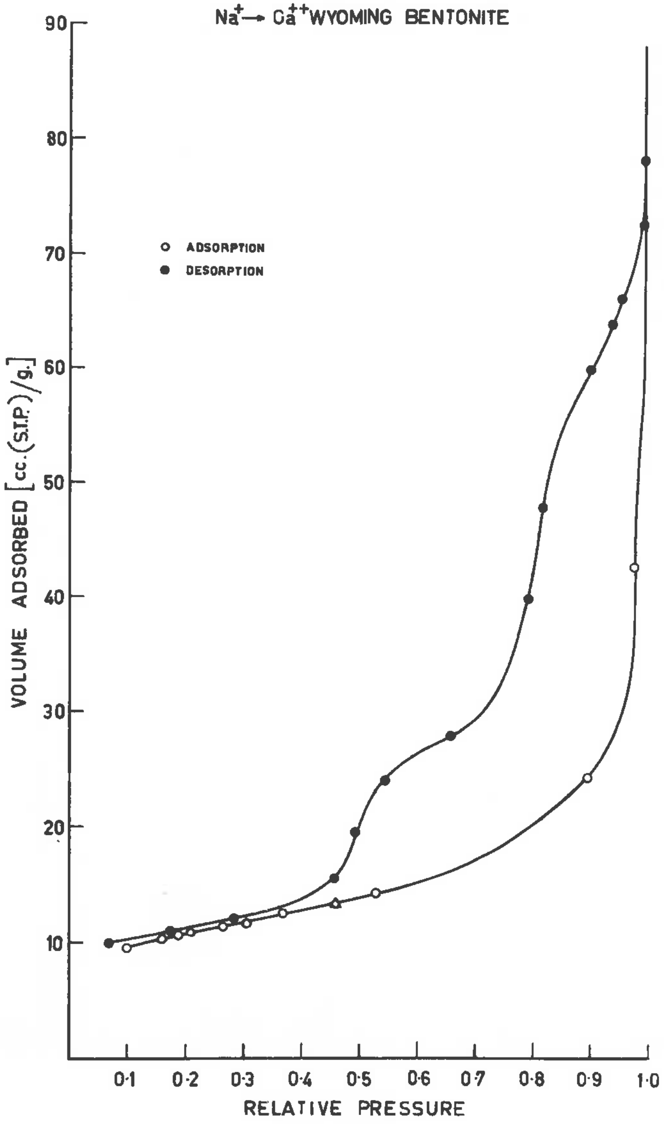


FIGURE 21.

below 33 Å equivalent cylindrical radius (0.75 relative pressure) than has the sodium → calcium clay. The isotherm for the sodium → calcium clay whilst being similar to that for the calcium clay is still intermediate between those for the calcium and sodium clays respectively. This variation in structural configuration coupled with the dependence of external surface area of the clay crystals on the nature of the exchangeable cation does seem to lead to the conclusion that the sodium montmorillonite lamellae are monodispersed in suspension and undergo a statistical reformation into crystals either on drying or in the presence of strong salt solutions.

A comparison between the structural status of the cores produced by the previous moulding process and that of the natural soil aggregates was made using the predominately illitic Urrbrae B clay. The nitrogen adsorption-desorption isotherms for the cores and natural aggregates of this material are shown in Figures 22 and 23 respectively and the differential plots are given in Figure 24. Although the total porosity of the cores is reduced in comparison with that for the natural aggregates, presumably by the removal of many of the coarse pores present in the aggregates, the general shape of the isotherms and consequently the distribution of plate separations appear to be very similar.

It is interesting to note that the shape of the nitrogen isotherm for the cores of this clay, used by Holmes (1955) in studying the swelling of moulded clay blocks, is very similar to that for the Willalooka illite. There is no indication of a shoulder at approximately 0.45 relative pressure as shown by Grundite illite and the montmorillonite

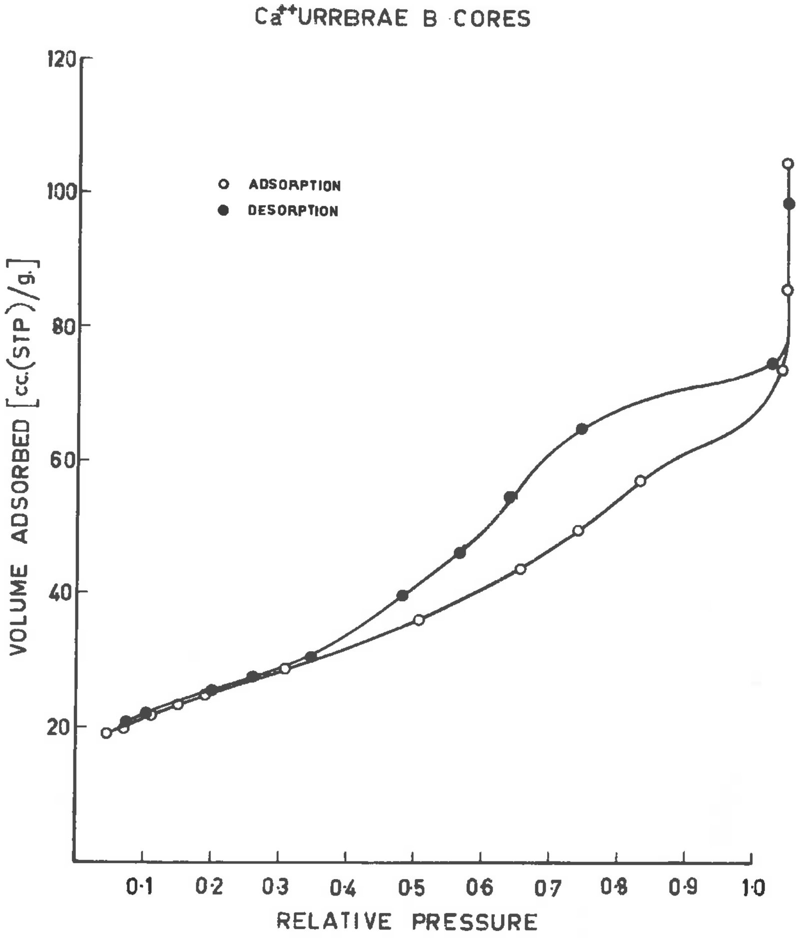


FIGURE 22.

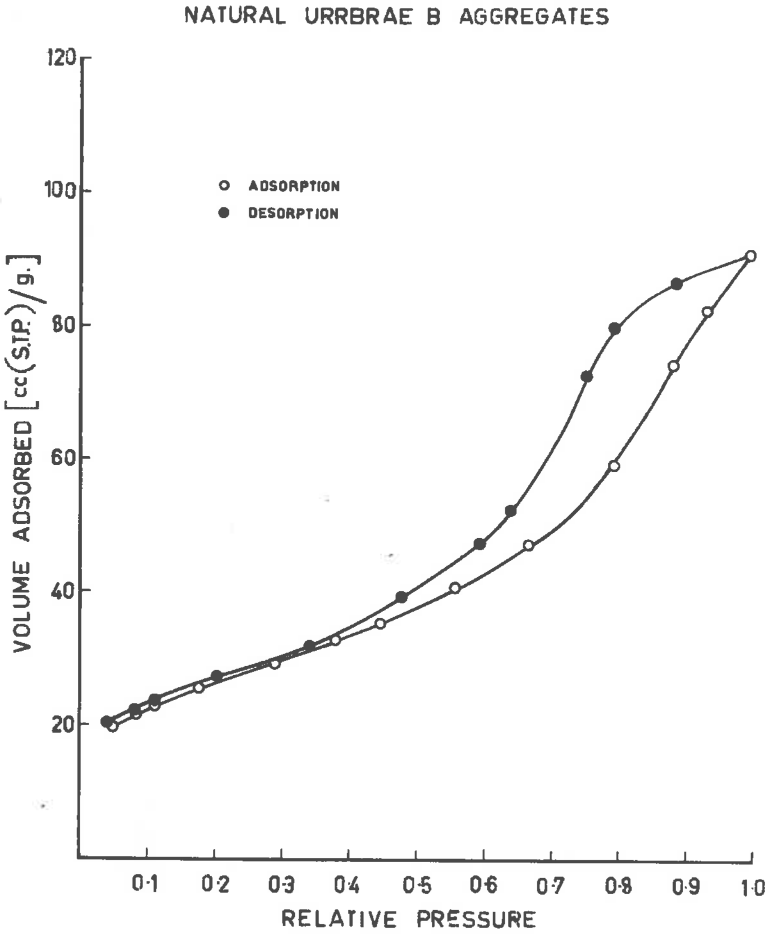


FIGURE 23.

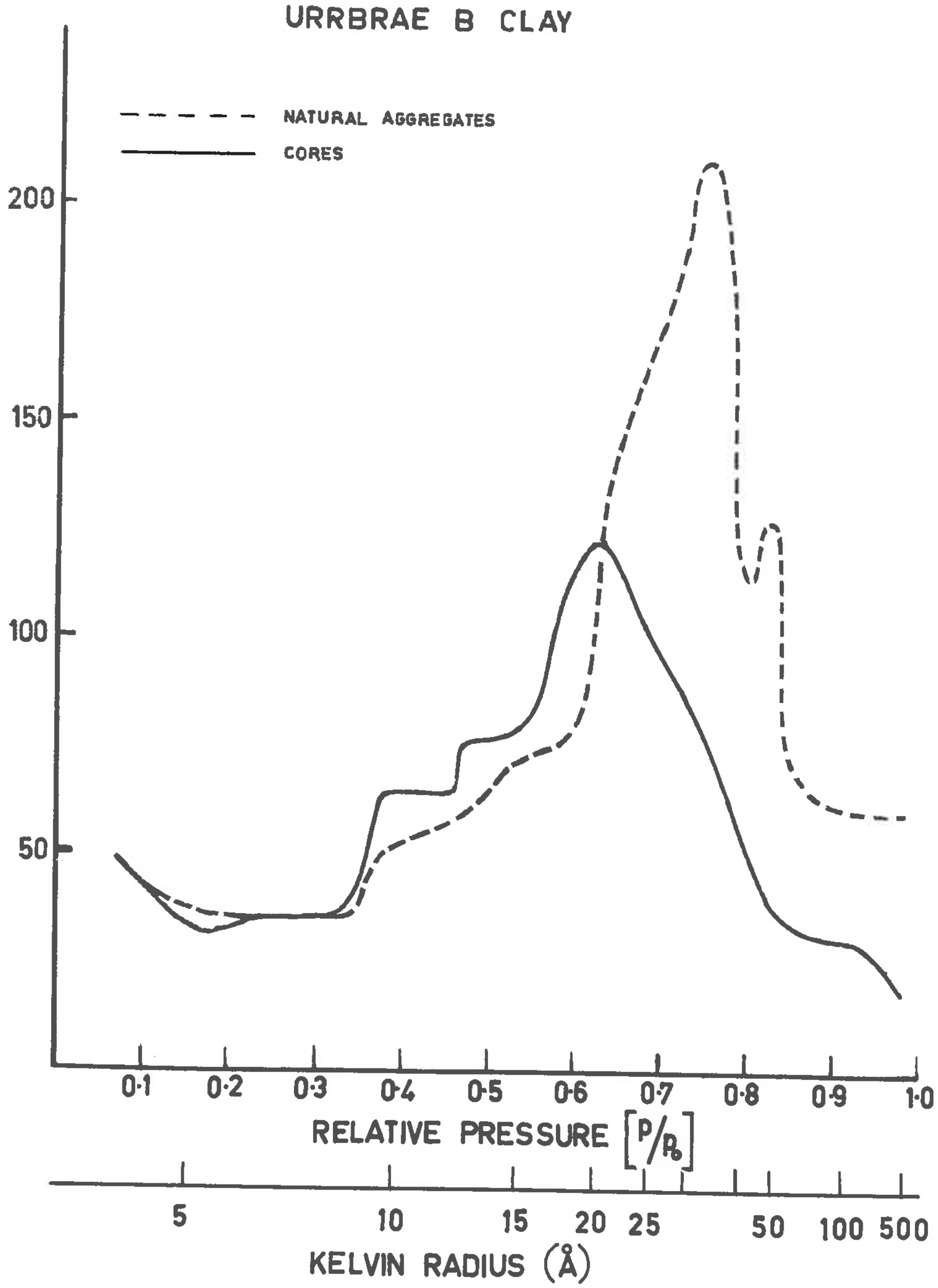

URRBRAE B CLAY
NATURAL AGGREGATES
CORES
200
150
100
50
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
RELATIVE PRESSURE [P/P₀]
5
10
15
20
25
50
100
500
KELVIN RADIUS (Å)

FIGURE 24.

clays and almost the entire porosity appears to be contained in separations of about 28 Å between clay plates. The total oven dry porosity of this clay 13.1 cc/100g, divided by its specific surface area 91 $m^2/g$ leads to an average value of plate separations equal to 28 Å as for the Willalooka illite. Consequently the Urrbrae B clay appears to have a similar highly oriented domain structure.

If it could be assessed accurately at just what point on the desorption isotherm the surface area obtained from the vapour-liquid interface formed was equivalent to the external surface area of the domains, an estimate of the average number of crystals forming a domain could then be obtained from the total surface area. However the range of pore dimensions apparently present within a domain, although relatively small, makes such a quantitative approach very difficult. For instance in the case of Willalooka illite the point at which the area of the liquid interface is equal to the external surface area of the domains, could equally well be considered to occur at any point on the desorption isotherm between those corresponding to the center of the peak on the differential curve (0.625 relative pressure) and the upper limit of this pore class represented by the completion of the differential peak (say 0.75 relative pressure). Although this only corresponds to a variation in pore dimensions from 20 to 33 Å equivalent cylindrical radius, the number of crystals per domain calculated by dividing the total surface area by $\frac{1}{\gamma}\int p\,dv$ at these points varies from about 7 to 40. In addition it is probable that such a simple model for domains is unrealistic in view of the probable interleaving and variation in size and shape of the crystals forming a clay mass.

## 6. ELECTRON MICROGRAPHS.

The development of the electron microscope has enabled the examination and direct measurement of objects whose dimensions lie between 10 Å and one micron. Most clay minerals fall within this range and considerable use has been made of this instrument in studying the morphology and structure of these clays.

A number of replica techniques for detailed reproduction of surface structures have been developed and in the hope of obtaining more information of the structural configuration and possible evidence of stacking of crystal units into domains, a number of electron micrographs of the fracture surfaces of the clay mineral cores were taken in collaboration with Mr. D. M. Hall of the Department of Scientific and Industrial Research, Dominion Physical Laboratory, New Zealand. These micrographs are shown in Figures 25 to 30. A three stage replica process was used to produce the replicas using polyethylene for the first stage and a carbon film for the last. The intermediate stage replica was shadowed twice with uranium. The first shadow was made at 20° to the plane of the replica and the second at 45°; the replica being turned 90° between the first and second shadow-casting. The replica was shadowed twice because of the rough nature of the surface. In the micrographs the shadows show as light areas and the direction of shadowing is indicated by an arrow. The thin dark lines indicate a vertical discontinuity and are due to the carbon film being opaque to the electron beam when edgewise on. The carbon film has a thickness of 200-400 Å. The heavy dark areas are due to some of the clay particles being transferred to the replica.

There are several areas in which the packing of the plate shaped particles into oriented groups can be distinguished. These appear as striated areas of alternate light and dark strips. Referring to Figure 28 for Willalooka illite for example, the area showing the clay particles stacked vertically appears in the centre of the micrograph and can be resolved be reference to Figure 31. The length of domain shown in this micrograph is approximately 10 microns, but it also extends just beyond the edge of the micrograph. The change in orientation of some of the particles can be clearly seen near the edge of this area.

Similar areas of this nature can be seen for the other clay species and bear some relation to the crystal size as is to be expected.

The size of the domain area for Willalooka illite (approx. 10 microns long) in comparison to the crystal size for this clay seems to indicate that a domain structure may consist not only of crystal sheets oriented and stacked but also interleaved across a considerable distance.

Additional evidence from the electron microscope of organization of clay crystals into oriented groups has been presented by Shaw (1942) and Bates (1958).

## FIGURE 25.

## ELECTRON MICROGRAPH OF FRACTURE SURFACE OF CALCIUM ROCKY GULLY KAOLINITE CORE

Magnification: X 10,400

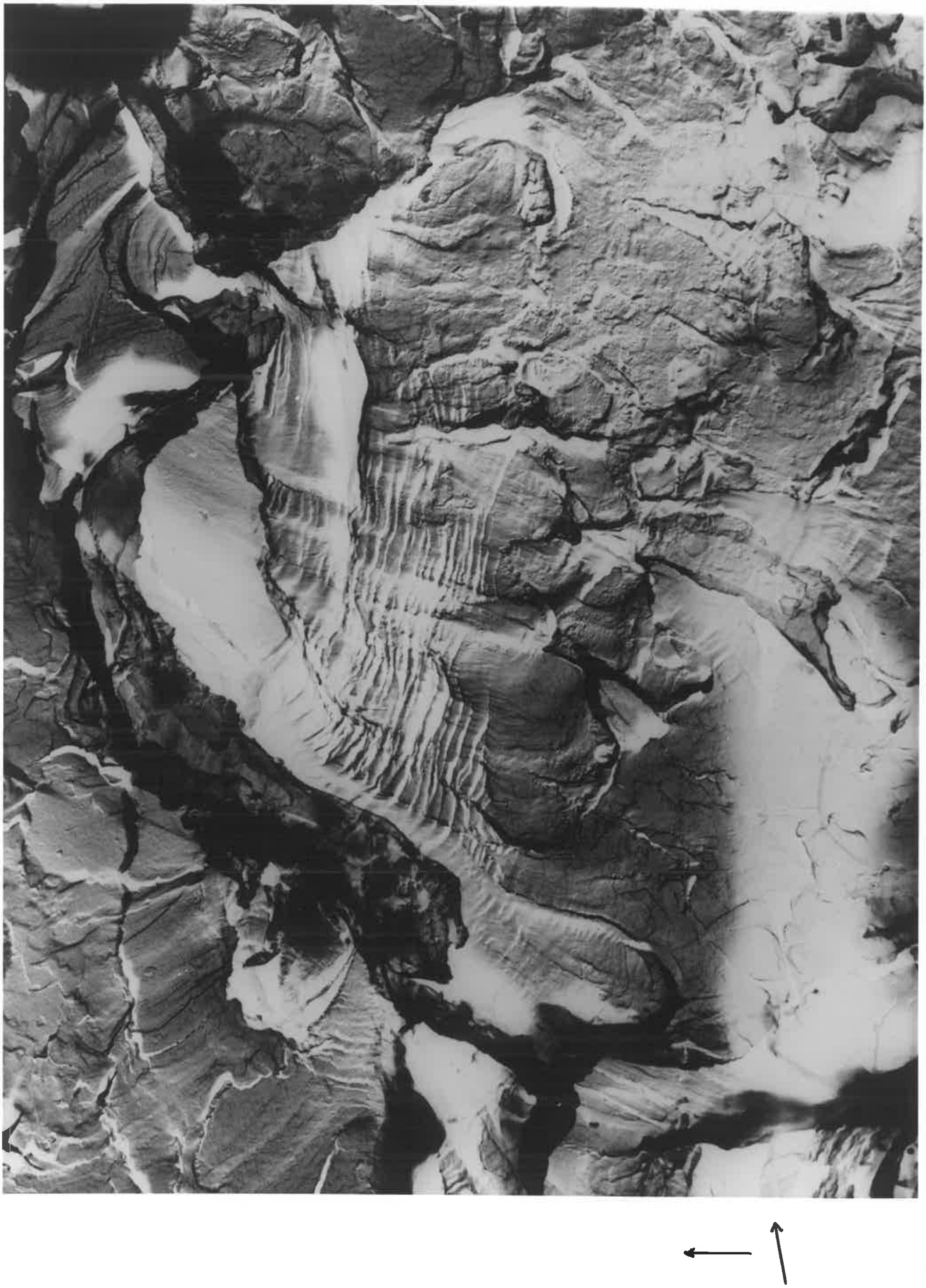
Reference Scale: 1μ ├──┤

# FIGURE 26.

ELECTRON MICROGRAPH OF FRACTURE SURFACE OF CALCIUM MERCKS I KAOLINITE CORE

Magnification: X 14,400

Reference Scale: 1µ



## FIGURE 27.

## ELECTRON MICROGRAPH OF FRACTURE SURFACE OF CALCIUM GRUNDITE ILLITE CORK

Magnification: X 10,400

Reference Scale: 1μ ├──┤

←

## FIGURE 28.

## ELECTRON MICROGRAPH OF FRACTURE SURFACE OF CALCIUM WILLALOOKA ILLITE CORE

Magnification: X 16,000

Reference Scale: 1μ

# FIGURE 29.

## ELECTRON MICROGRAPH OF FRACTURE SURFACE OF CALCIUM WYOMING BENTONITE CORE

Magnification: X 16,800

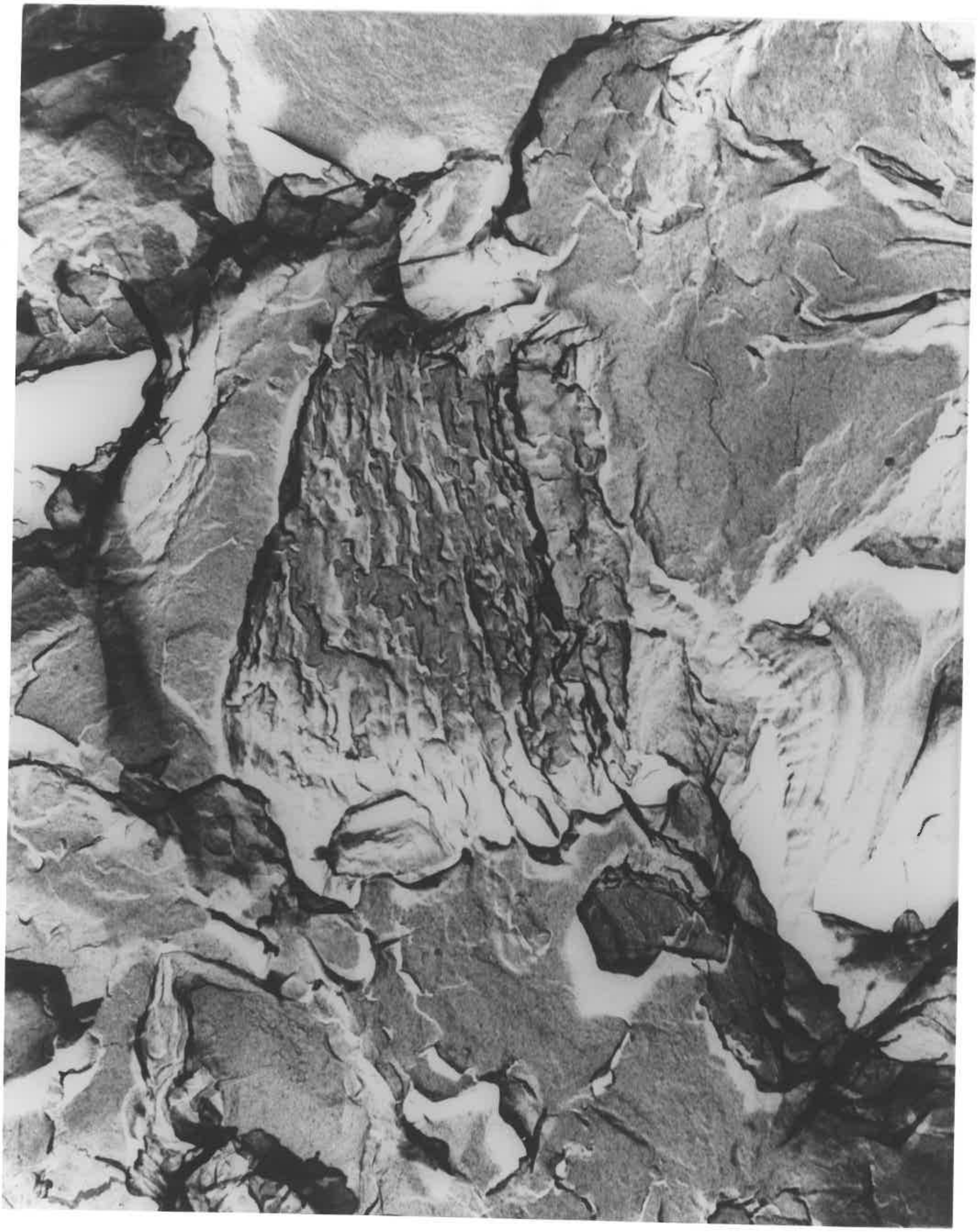
Reference Scale: 1µ

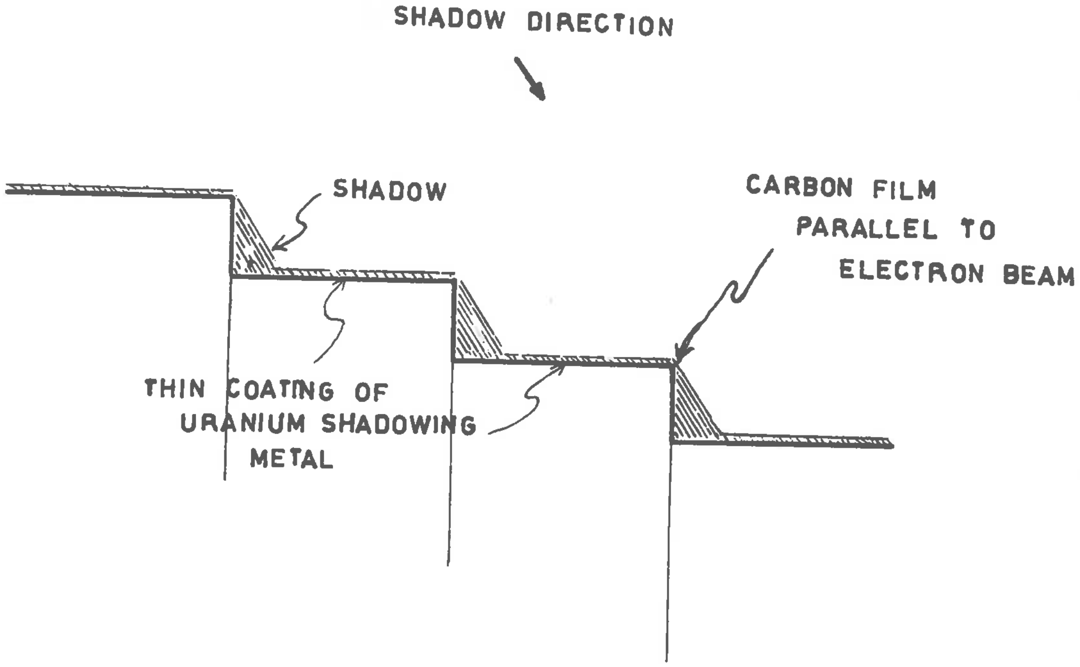
## FIGURE 30

## ELECTRON MICROGRAPH OF FRACTURE SURFACE OF CALCIUM REDHILL MONTMORILLONITE CORE

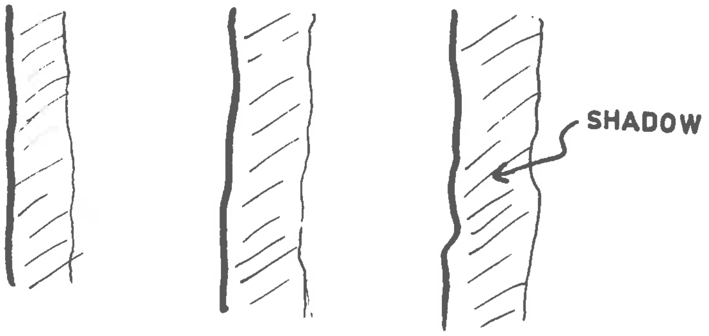
Magnification : X 24,000

Reference Scale : 1μ





ELEVATION VIEW OF CROSS SECTION OF CLAY



MICROGRAPH

FIGURE 31.

## SECTION 3

## ANALYSIS OF WATER CONTENT-SUCTION DATA IN TERMS OF FILM-THICKNESS DEVELOPED ON CLAY SURFACES

The water content of a clay mass at any particular suction is a function of both the adsorption capacity of the clay surface and the structural status of the clay mass. Swelling accompanying surface adsorption and hydration of exchangeable cations has been adequately demonstrated by X-ray workers as outlined in Section 1. The effect of structural status is evidenced to some extent by the existence of hysteresis in the clay water-energy relationship even in the saturated state as has been observed by many workers (Haines, 1923; Croney and Coleman, 1954; Holmes, 1955; Warkentin, Bolt and Miller, 1957 etc.). In particular Croney and Coleman demonstrated that although a thoroughly slurried clay mass described a continuous drying curve to complete dessication (normal consolidation curve) on the application of progressively higher suctions, this curve was not retraced on decreasing the suction. Rewetting and subsequent drying from different positions on the normal consolidation curve resulted in a series of closed hysteresis loops. However, it was found that a unique water content-suction relationship could be obtained by continual disturbance of the clay mass during the wetting and drying processes. Parry (1959) has recently attempted to explain the variation from this unique line (termed critical voids ratio line) and the return to it on the application of shearing forces in terms of latent interparticle forces of molecular origin.

As a purely osmotic phenomenon the development of the water film on a clay surface should be completely reversible and for any value of the applied suction, both hydrostatic and osmotic, it seems reasonable to expect that a unique value for water film thickness or half plate separation should be obtained. The existence of potential barriers such as observed by Norrish (1954) at low plate separations for the intra-crystalline swelling of montmorillonite clays may be more general than has hitherto been recognized and could also contribute to hysteresis effects. However, the nature of the irreversible hysteresis observed in the saturated state, seems to indicate that structural alterations due to particle readjustment are of major importance in determining this hysteresis (Schofield, 1935). Consequently before any attempt can be made to interpret the water content of a clay-water system in terms of the water film thickness developed on the clay surface, a satisfactory model for the structural configuration of the clay matrix is obviously necessary.

In the dispersed state the clay crystals may be considered as randomly placed with respect to each other and behaving almost independently as depicted in Figure 32 (a). As the water content is decreased inter-particle forces become operative and in addition mechanical inter-actions between the solid particles leading to the formation of a loosely packed, randomly oriented, gel network such as illustrated in Figure 32 (b) are possible. Various workers (McDowell and Usher, 1951; Broughton and Squires, 1936; Goodeve, 1939; Schofield and Dakshinamurti, 1948; Van Olphen, 1951, and McEwen and Pratt, 1957) have postulated the formation of

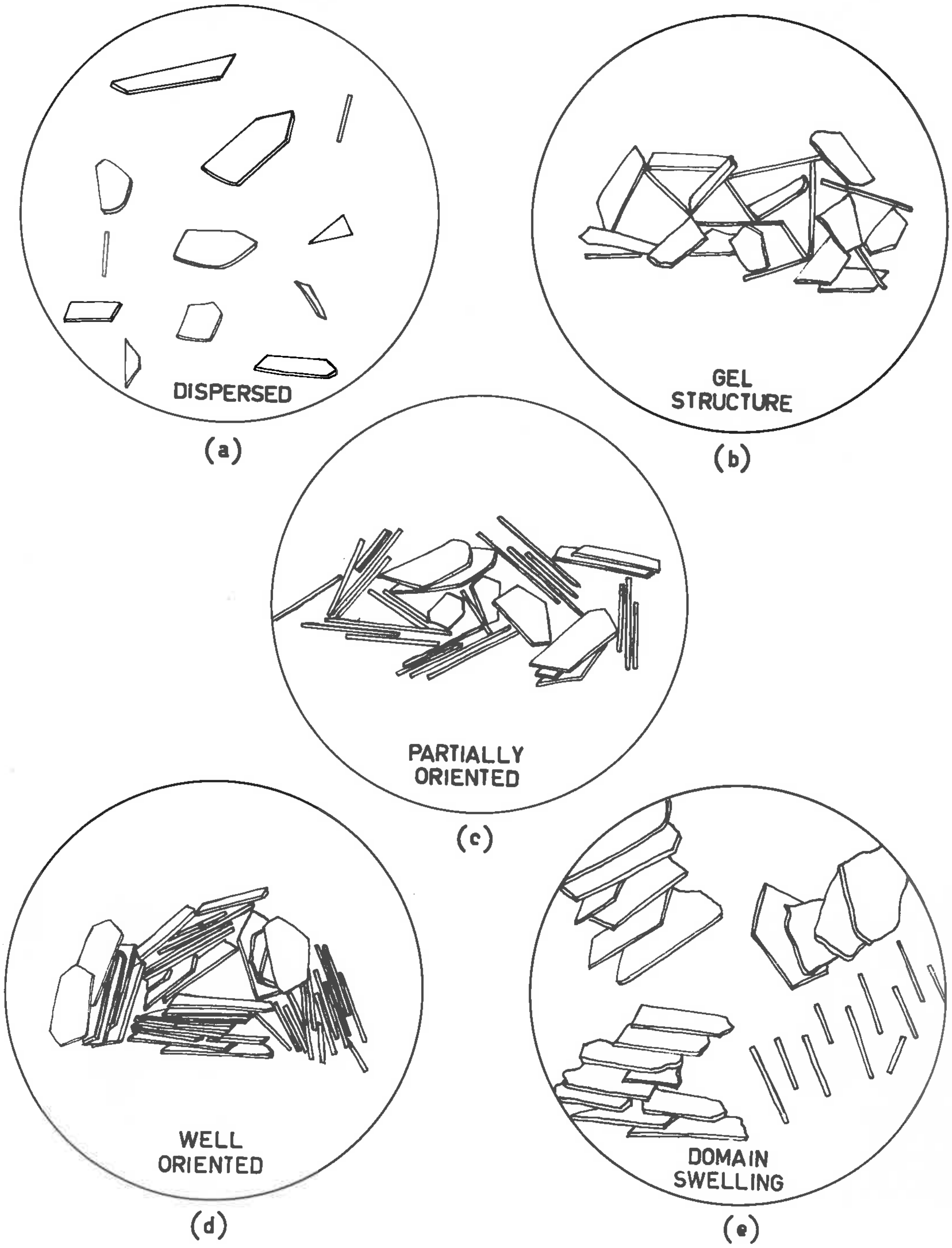


FIGURE 32.

DIAGRAMMATIC - Separations Exaggerated in Relation to Particle Dimensions.

"scaffolding" or "house of cards" structures by rod and plate shaped particles either by edge to edge or edge to face contacts to explain thixotropic behaviour and it is apparent that such networks could enmesh and return large quantities of water.

On further drying or alternatively on increased compression of the clay water system, the crystals would tend to take up positions of minimum potential energy with respect to each other and this would be achieved mainly by oriented stacking. This follows from mechanical stability considerations and also from osmotic considerations, since a variation in repulsive potential would exist at the mid-plane between opposed plates which are not completely aligned. The extent to which this oriented stacking occurred would be determined largely by factors such as crystal size and shape, rapidity and degree of drying, degree of flocculation determined by the electrolyte concentration present, applied pressure and possibly the physico-chemical nature of the clay surfaces. Dependant on these factors the configuration of the clay matrix could therefore be expected to vary between the completely disorganized state and a high degree of orientation as illustrated in a simplified manner by Figure 32(b) to 32(d). This degree of orientation and consequent variation in volume of water simply enmeshed within a gel-like structure, as compared with that associated with clay surfaces, may well explain the nature of the rebound curves observed on rewetting from different positions on the normal consolidation curve (Croney and Coleman, 1954; Warkentin, Bolt and Miller, 1957) and the subsequent behaviour of the clay-water mass on the application of shearing forces (Parry, 1959).

As the clay-water system dried from a situation approaching the gel state, the formation of domains of oriented crystals and the subsequent re-orientation of these domains to positions of minimum potential energy would cause the volume of enmeshed water to decrease continually. On rewetting from positions on the normal consolidation curve with different volumes of enmeshed water the domains may retain their entity and swell as such, causing the pore volume to swell proportionately to the overall volume of the clay mass thus giving rise to a series of rebound curves as observed by Croney and Coleman and Warkentin, Bolt and Miller. This also enables the same water content (voids ratio) to be obtained with quite different structural arrangements within the clay mass and must of necessity result in appreciable differences in the strength of the soil structure depending on the ratio of the water held in pores to that held within the domains. The application of shearing forces or mechanical disturbance to a gel structure would tend to accelerate its destruction and increase the particle alignment thus giving rise to the decrease in volume observed for clay masses on the normal consolidation curve in these circumstances. Beyond a certain degree of alignment into domains however, the application of shearing forces or mechanical disturbance may tend to either disrupt the domains themselves or if they are strong enough to resist such disruption, the tendency may be to increase the volume between adjacent domains. Either process could lead to the resultant increase in volume and suction observed for overconsolidated clays in these circumstances. The critical voids ratio line may therefore be considered as indicating the equilibrium position between complete aligmment and completely random packing of the clay particles on disturbance for each particular suction value.

The form of each of the series of essentially reproducible hysteresis loops described on successive wetting and drying from various points on the normal consolidation curve as illustrated by Croney and Coleman can be attributed to the existence of slight differences in swelling behaviour between domains of crystals, giving rise to a large number of groups in a metastable state thus conforming to the domain theory of hysteresis as postulated by Everett and Whitton (1952).

In view of the great diversity possible in the fortuitous structure developed on drying a clay from the suspension or gel state it is apparent that the interpretation of water content-suction data obtained in this manner in terms of water film thickness developed on the clay surfaces is unsound.

On repeated wetting and drying, however, the clay mass tends to describe what may be termed a final reproducible hysteresis loop in which the clay particles appear to have reached a state of maximum practical orientation. In order to obtain this reproducible hysteresis loop for a clay material it is necessary to dry it to its shrinkage limit. It therefore seems possible that in this state the degree of fortuity in the structural status of the clay mass would be reduced to a minimum and hence interpretation of total water content on wetting in terms of surface adsorbed and pore enmeshed water would be greatly facilitated, provided the particle arrangement was satisfactorily defined for a particular clay. For this reason the techniques (as described in Section 4) using small compressed and predried cores of the clay materials to study swelling were adopted.

It is apparent from the investigations carried out in Section 2 of this thesis and those of other workers that varying degrees of orientation of crystal plates with respect to each other are present in dry clay masses. A simple picture of the clay matrix as a porous media consisting of the clay crystals oriented on a microscale into small packets or domains may therefore be assumed. In this regard it is interesting to note that Terzaghi (1956) has drawn attention to the fact that the bulk of the clay fraction of natural clay soils, determined by machanical analysis, consists of particles of the order of magnitude of 1μ which in view of the much smaller crystal size must therefore consist of micro-aggregates or clusters of a great number of clay crystals. It seems likely that these clusters are in actual fact the oriented groups previously evidenced and since the term "domain" has been used in the theory of magnetism to infer an aligned state it may be a more appropriate term. These domains of orientated crystals can in a general way be regarded as analogous in structure to single crystals of montmorillonite and since they appear capable of retaining their entity even in suspension, must possess appreciable internal strength. From the electron micrographs and the nitrogen adsorption data the true clay status is obviously far more complex than the above simple model but it may nevertheless serve as a reasonable first approximation.

If this model is accepted it seems reasonable to assume that on initial swelling of the clay media from the dry state the pores within the clay matrix will expand as the overall volume of the clay-water system increases (Figure 32(e)) in much the same way as the internal volume of a metal pipe expands on heating. The extent to which this proportional expansion of pores would continue before structural rearrangement of particles and internal accommodation of inter and intracrystalline (where applicable) swelling disrupts the original porous structure is difficult to say. This would undoubtedly depend on the magnitude of the pores and the nature of their construction. However, the fact that the clay mass reaches a state in which it will describe the same hysteresis loop on successive wetting and drying does seem to indicate that for any one particular clay there is a unique "pore" volume which is inherent for that particular material. This "pore" volume may be either some function of the original oven dry porosity or may simply arise from a gel structure which forms subsequently. Therefore to divide the total water content by the specific surface area of the clay must in all but exceptional circumstances provide an overestimate of the actual water directly associated with the clay surfaces, since this procedure attributes water simply enmeshed in the porous structure to be surface retained. This procedure would only be valid in the case of a clay mass with complete parallel orientation of particles with respect to each other and this is a highly improbable state for a natural clay mass although the error in accepting this situation for certain highly oriented clays may not be large.

For clay materials which do not exhibit extremely large water uptakes and in which therefore considerable particle rearrangement is unlikely, it seems a reasonable procedure to consider that the water not held directly on the clay surfaces should bear some relationship to the oven dry porosity. An increase in pore volume on swelling, proportional to the overall volume of the clay-water mass, as previously suggested, may be appropriate in these circumstances. The calculation of surface film thickness in the saturated state would then be made as follows :

$$\text{Swollen Porosity} = \text{Oven Dry Porosity} \times \frac{\text{Total Volume of Clay - Water Mass}}{\text{Apparent volume of Oven Dry Clay}}$$

and hence

$$\text{Surface Film Thickness} = \frac{\text{Total Water Content} - \text{Swollen Porosity}}{\text{Specific Surface Area.}}$$

One obvious objection to this model of course, is that a certain proportion of the oven dry porosity will arise from incomplete contact of parallel crystal cleavage faces in the dry state. On the adsorption of water this volume would be occupied by water directly associated with the clay surfaces. From Section 2 of this thesis such separations would appear to contribute the major part of the oven dry porosity for certain of the clays examined, in particular Willalooka illite and Urrbrae B clay. The subtraction of a proportionately swollen total pore volume from the total water content should therefore in the absence of any complications such as the formation of thixotropic gel structures, lead to an underestimate of the correct film thickness.

Consequently some idea of the limits between which the correct film thickness might be expected to lie should be obtained by application of these calculations to a clay matrix previously adjusted to the final reproducible hysteresis loop. However, the possibility of the formation of thixotropic gel structures and consequent reorganization of structure even on controlled wetting from the dry state has also to be considered and may invalidate this computation of structure enmeshed water on the basis of the oven dry porosity.

These considerations have been used in the following section to analyse the solution content-energy data obtained.

# SECTION 4

# DETERMINATION OF WATER CONTENT-SUCTION RELATIONSHIPS FOR CLAY-MINERAL SYSTEMS

## 1. EXPERIMENTAL

### 1.1 Apparatus.

A range of hydrostatic suctions from zero to complete dessication was obtained using the following apparatus.

### 1.1.1. Pressure plate apparatus (pF 0 - 2.8)

Figure 33 shows one of the battery of ceramic perspex cells used for the low pF range. The reservoir beneath the ceramic plate is connected to a small constant head of liquid and a constant pressure of nitrogen gas is maintained in the perspex dome above the ceramic plate by means of a gas cylinder and a series of bubble towers (Figure 34). The ceramic plate (pore diameter < 1μ) is sealed into the bottom perspex plate with "Araldite" casting resin D and Neoprene rings provide an excellent seal between the two sections of perspex. The pressure plate is only open to the atmosphere during sampling thus reducing evaporation losses to a minimum. This is of considerable importance when electrolyte solutions and not distilled water are being used. The gas cylinder-bubble tower system for obtaining the required water suction on the clay materials up to 700 cm. suction has the advantage of being less complicated and more compact than systems working on a vacuum principle (Holmes, 1955) which require an extensive vacuum pump-reservoir-electrical cut off arrangement. The equivalence of the two methods was

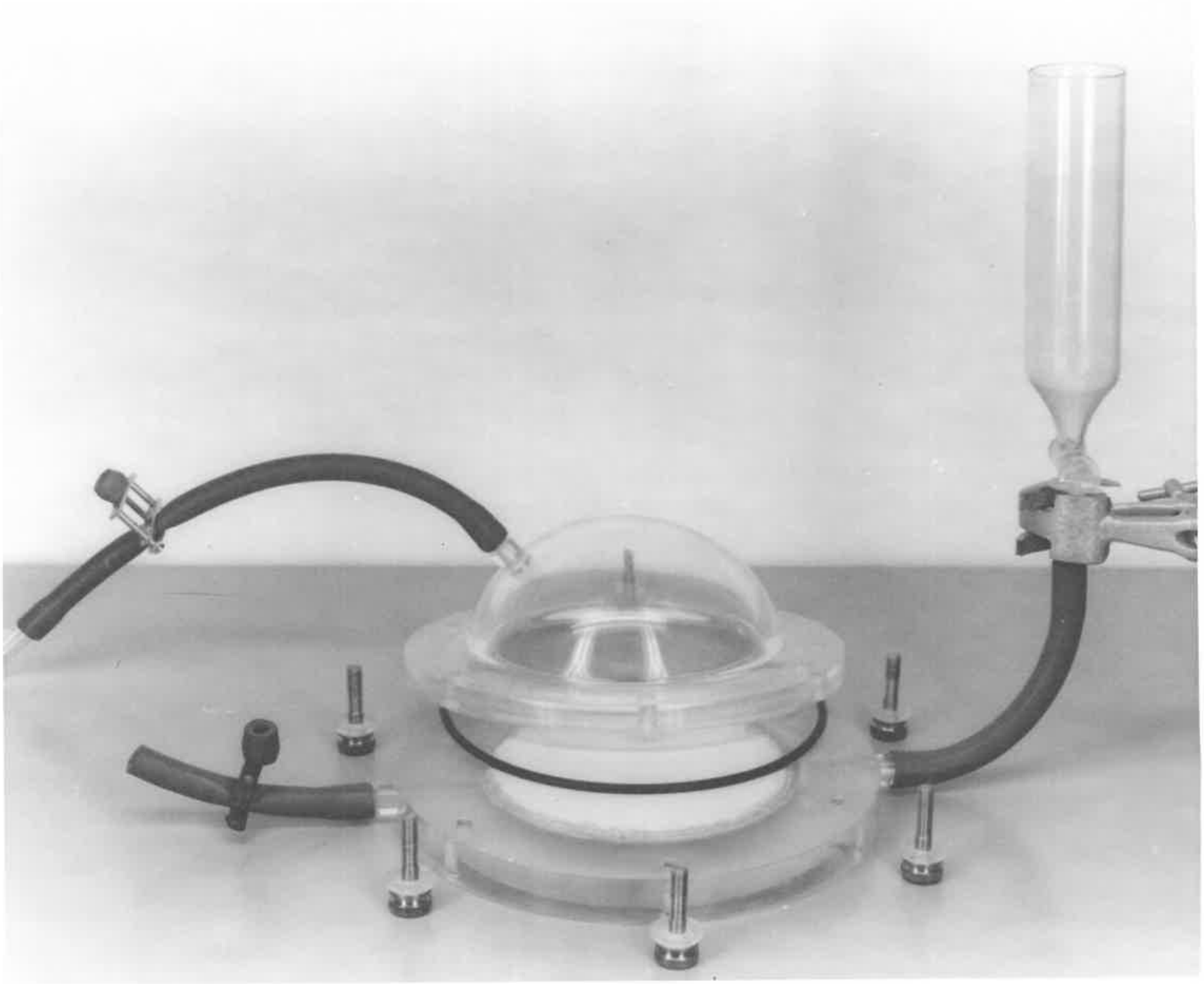


FIGURE 33.

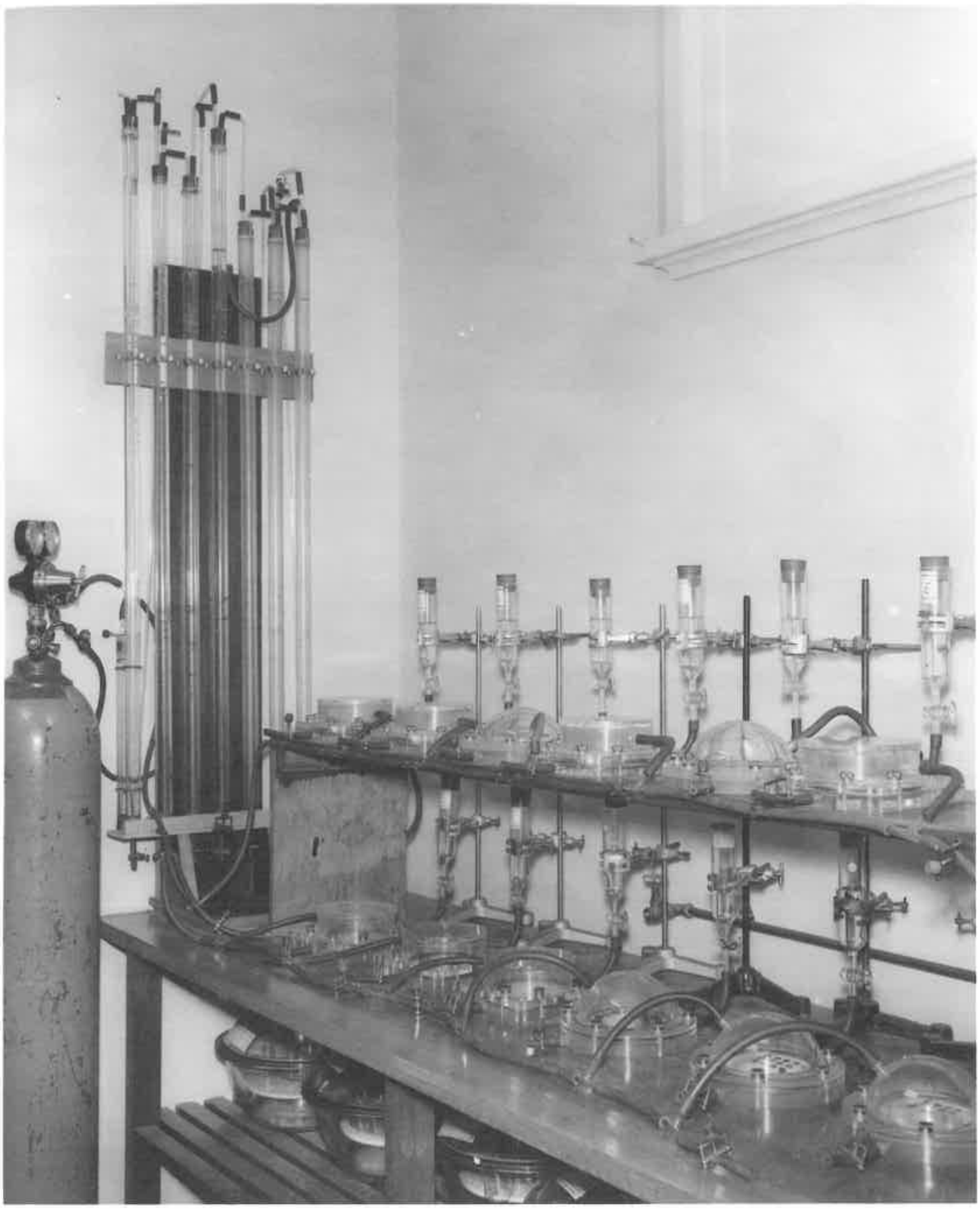


FIGURE 34.

verified by comparison of preliminary data obtained for clay materials by both methods.

Before releasing the pressure in the chamber, prior to sampling, the tap connecting the porous plate to the solution reservoir is closed to prevent the flow of solution from reservoir to plate during sampling.

### 1.1.2. Pressure Membrane Apparatus (pF 3 - 5)

Figures 35 and 36 show the two designs of pressure membrane apparatus used to obtain the middle pF range. The low pressure membrane (Figure 35) is an improvement on the apparatus described by Richards (1947), incorporating O range seals between sections. The high pressure membrane (Figure 36) was specifically designed to enable pressures up to 200 atmospheres to be exerted above the cellophane membrane. Both designs have an inlet and an outlet to the space below the membrane to enable it to be flushed with the particular solution in use to prevent the formation of air bubbles and the possibility of drying out of the membrane through evaporation. The membrane of "Visking" cellulose casing was soaked overnight in the solution in use and allowed to equilibrate with the required pressure in the chamber before the samples were placed on it. The use of the high pressure membrane enabled some overlap between the liquid and vapour phase transport points to be obtained.

### 1.1.3. Vapour Pressure Determinations (pF 4.7 - 6.5)

In this range the clay cores were placed in dessicators over saturated solutions of the following salts and equilibrium was accelerated

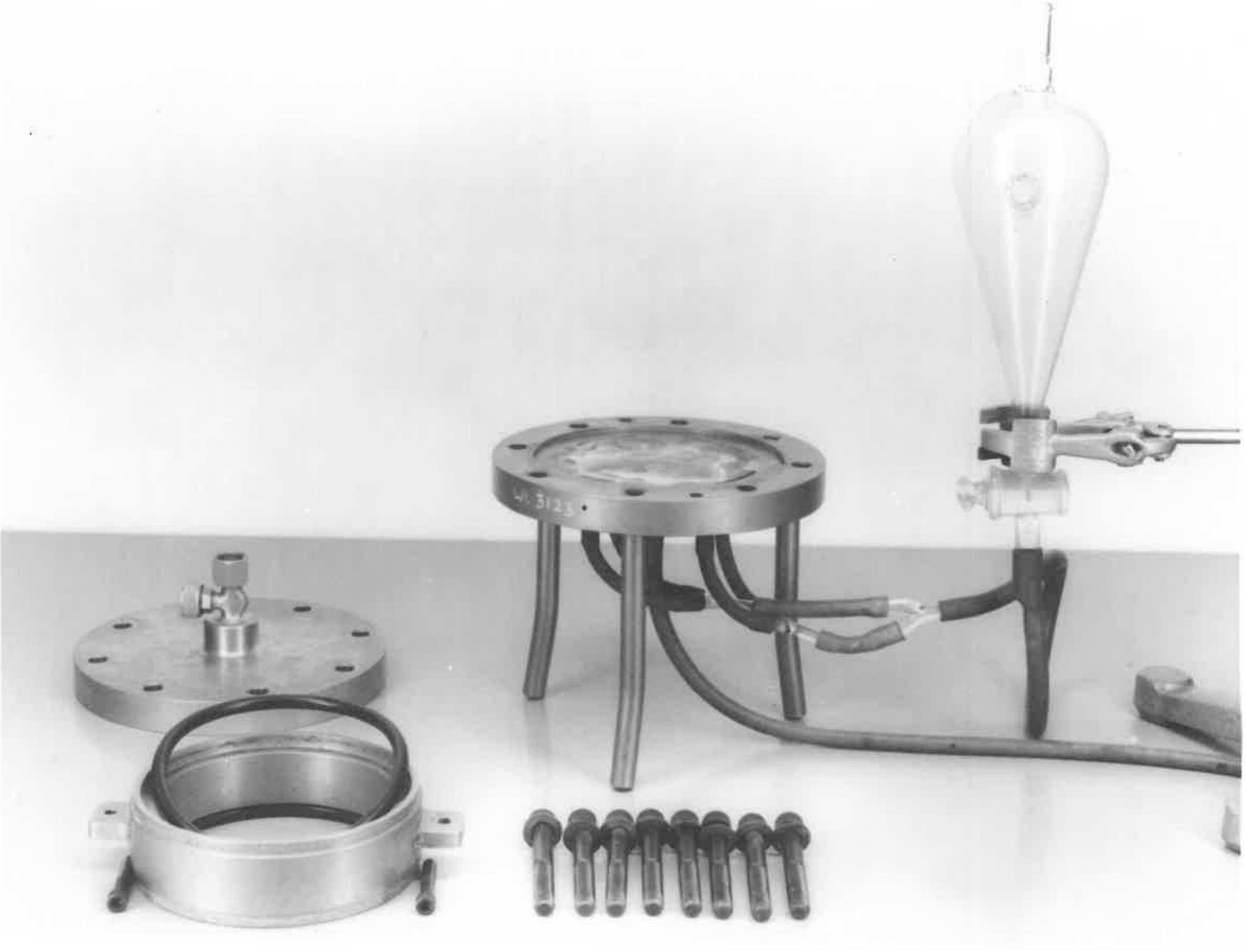


FIGURE 35.

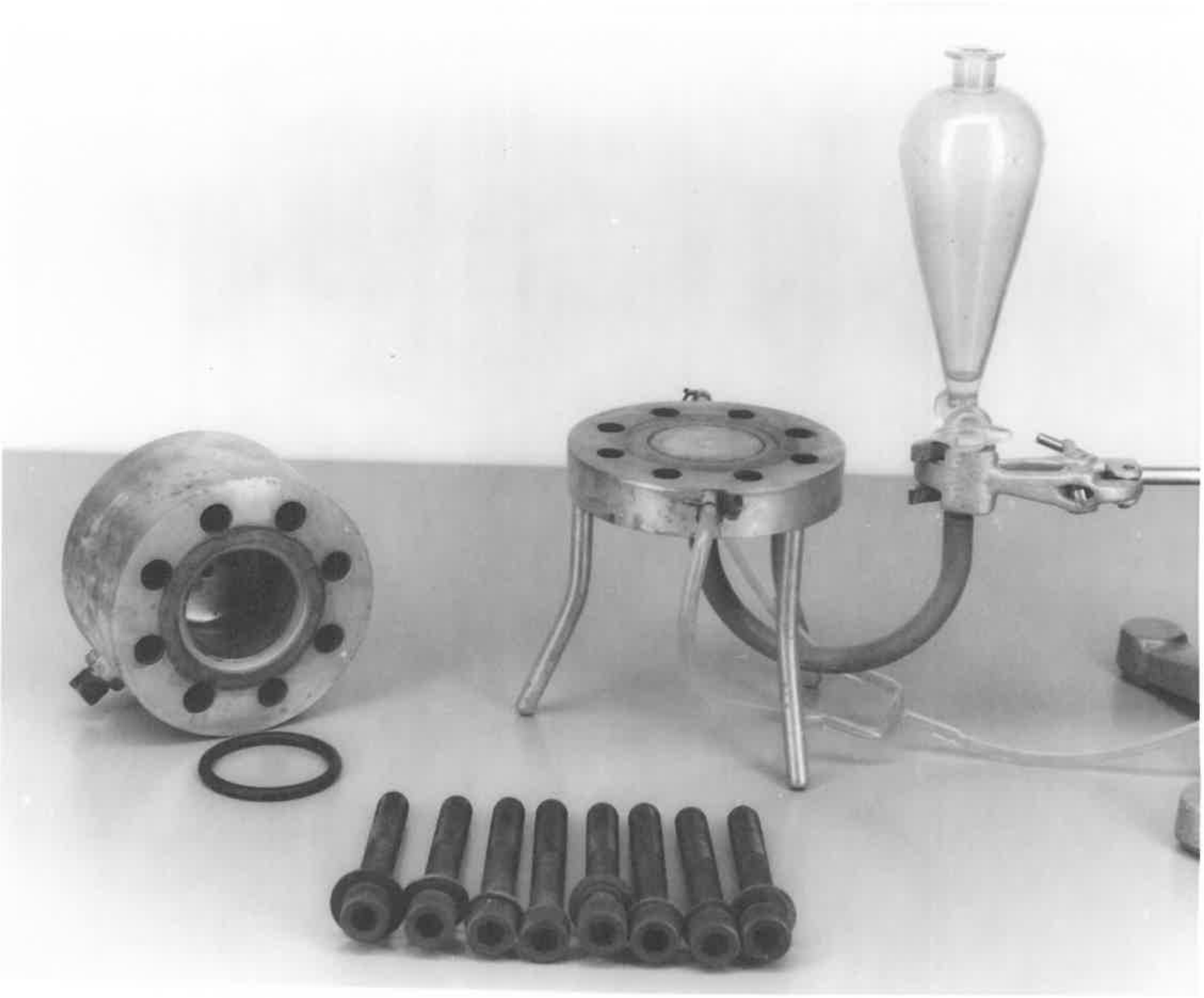


FIGURE 36.

by evacuation on a water pump.

| Solution | Relative Vapour Pressure | pF Equivalent |
|---|---|---|
| $K_2SO_4$ | 0.96 | 4.7 |
| NaCl | 0.76 | 5.6 |
| $Ca\ (NO_3)_2$ | 0.51 | 6.0 |
| $MgCl_2$ | 0.32 | 6.2 |
| $CaBr_2$ | 0.19 | 6.4 |
| $ZnCl_2$ | 0.10 | 6.5 |

Complete dessication was obtained by evacuating the cores in a dessicator over phosphorus pentoxide powder by means of a water pump.

### 1.1.4. Temperature Control.

The water suction apparatus previously described were set up in a constant temperature laboratory maintained at 20°C ± 1/4°C.

### 1.1.5. Volume Measurement.

In the liquid transport range pF < 4 the volume displacement method (McIntyre and Stirk, 1954) was used for volume determinations since the cores were found to be saturated over this range. In the higher pF range the cores were in various stages of saturation and the total volume of the cores were determined from direct measurements of the dimensions using either a travelling microscope or a micrometer. Water content changes during this procedure were found to be insignificant. To increase the accuracy of the volume measurements 400 mg cores were used.

For volumes of the order of 0.2 cc both methods gave better than one per cent. accuracy.

### 1.1.6. Chloride determination.

Chloride determinations were carried out by the electrometric titration method (Kolthoff and Kuroda, 1951) using a quinhydrone half-cell, silver-silver chloride electrode in conjunction with a Cambridge millivolt meter.

## 1.2 Procedure.

After manufacture the cores were wet in stages (pF 4.7 → 2.8 → 2.0) to pF 2 and then dried via 0.75 and 0.19 relative vapour pressure to complete dessication over phosphorus pentoxide before determination of the isotherms. This step was taken to allow the clay matrix to adjust to a natural state from any structural characteristics enforced by the manufacturing procedure and to examine the effect of successive wetting and drying cycles on the hysteresis loop described by the clay cores. Varying but small decreases in water content between the first and second wetting to pF 2 were observed. For the divalent montmorillonites these differences were quite significant but further wetting and drying cycles produced little change. For the monovalent montmorillonites which exhibit large swelling and the remaining clays the differences were of little significance.

The approach of a disturbed clay mass to the final reproducible hysteresis loop is undoubtedly an asymptotic one but for all practical purposes the clay cores after describing one wetting and drying loop after the initial compression process can be considered to closely approximate this state of minimum potential energy. This preliminary wetting was carried out for all cores except the magnesium saturated clays for which the curves shown represent the first loop described after drying the manufactured cores over phosphorus pentoxide powder.

The water content-energy relationships were obtained by taking a sufficient number of cores and bringing duplicates to set values of pF. 200 mg cores were used in general for equilibrium water content determinations and 400 mg cores for volume determinations. In practice even with such small weights of material it was found necessary to wet and dry in several stages to prevent disruption of the cores due to differential swelling, particularly in the case of the montmorillonite clays. This procedure enabled the same point to be checked several times whilst taking considerably less time than the procedure wherein individual cores are allowed to come to equilibrium at each point on the wetting and drying isotherms before proceeding to the next point. The variation between cores on the second wetting was very small, the differences in water content between duplicates at pF 1 being, in general, less than one per cent. of the total water content.

In the case of the electrolyte solutions the determinations were confined to the liquid transport range since the vapour pressure measurements involve a continuous variation in osmotic pressure component of the total pressure as the water content changes, for all but salt free clays. Furthermore the effect of electrolyte is not important below pF 4.5.

It was found necessary to pre-determine the oven dry weights of the clay cores before wetting with the salt solutions, particularly in the case of the strong calcium chloride solutions, since oven drying at 110°C was insufficient to completely remove the water of hydration from the salt in the clay and this factor produced significant variations in the oven dry weights. This was done by first weighing the cores in equilibrium over phosphorus pentoxide and adjusting for the water content determined on the oven dry basis.

The density of the strong salt solutions increased considerably from that of distilled water and to make the results for different concentrations directly comparable the solution contents are given in volume of solution absorbed per 100 grams of oven dry clay. This also facilitates the calculation of film thicknesses developed on the clay surfaces. The volume of solution was obtained by dividing the weight of solution by the appropriate solution density, 1.33 gm/cc and 1.09 gm/cc for four molar and molar calcium chloride respectively and 1.04 gm/cc for molar sodium chloride solution. Volume measurements on the clay cores saturated with these solutions, confirmed these values for solution densities for the absorbed solution within experimental error. For the remaining solutions the assumption of a solution density equal to unity leads to insignificant error.

The solution contents are plotted against pF. The pF values do not indicate the total lowering of the free energy due to both hydrostatic and osmotic components as initially defined by Schofield (1935) but only that component arising from the applied hydrostatic suction.

In several instances the values of solution content on drying to various suctions from the suspension state were obtained to provide a comparison with the behaviour of the clay cores wet from the dry state. Suspensions of different electrolyte concentration were obtained by shaking the powdered homoionic clays with distilled water for two days on a Griffin and Tatlock Microid flask shaker and then adjusting the concentration by the addition of the appropriate electrolyte. The suspensions were dried in $1\frac{1}{2}$" perspex rings sealed onto the ceramic plates or cellophane membrane by a thin layer of vaseline. Sampling was carried out from the centre of the ring to avoid contamination by the vaseline.

### 1.3 Equilibrium.

Time for equilibrium varied between the clays and since the montmorillonites required the longest period they were used to establish a criterion for equilibrium. The approach to equilibrium is asymptotic but in general for the 200 mg cores, 15 and 25 days were found to be satisfactory times for the divalent and monovalent clays respectively in the liquid transport region. In the vapour transport region the samples were allowed to attain constant weight. This was usually reached within 7 days for all but the 0.96 relative vapour pressure dessicator where several weeks were sometimes required and equilibrium was not as satisfactory as for the other points. Typical approach to equilibrium curves for sodium Wyoming Bentonite and Redhill montmorillonites are shown in Figure 78.

## 2. RESULTS

### 2.1 Kaolins.

### 2.1.1. Distilled Water.

The water content-suction relationships obtained for Rocky Gully and Mercks I kaolinite when saturated with various cations, are shown in Figures 37, 38, and 39 to 42 respectively. The Rocky Gully kaolinite cores describe approximately the same hysteresis loop regardless of the exchangeable cation present and behave rather like constant structured materials the majority of whose pores fill and empty between pF 5.0 and 5.25 corresponding to equivalent cylindrical pore radii in the vicinity of 100 Å as indicated by the nitrogen studies. At lower pF values there is a relatively small swelling accompanied by a narrow hysteresis. Mercks I kaolinite on the other hand despite its very much smaller specific surface area exhibits considerable swelling and an appreciable dependance of water content at low pF values on the exchangeable cation present. There is a large hysteresis effect evident between pF 1 and 5 possibly indicating considerable readjustment of particles with respect to each other.

The behaviour of these two clays is therefore in the reverse order to that to be expected in relation to their specific surface areas since Rocky Gully kaolinite has more than three times the specific surface area of Mercks I kaolinite. From this it appears that the swelling of the Rocky Gully cores is subject to some restriction not in

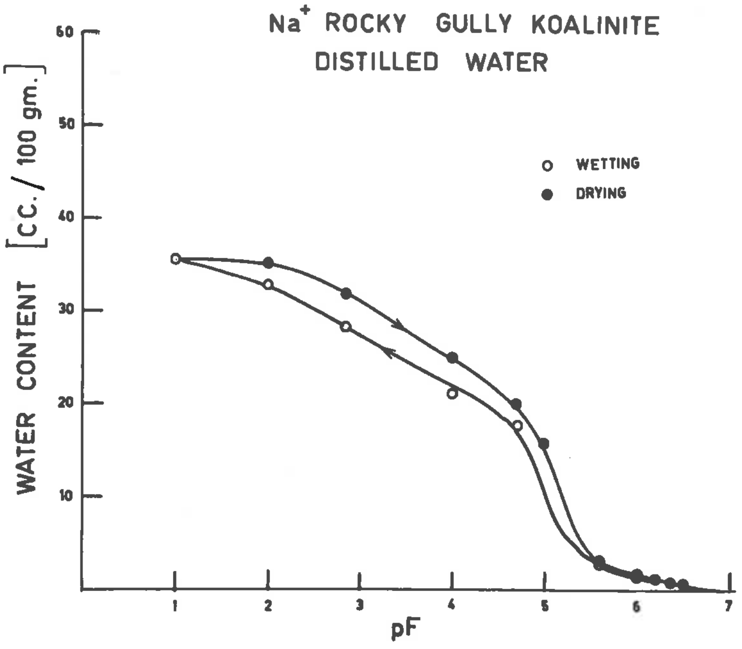


FIGURE 37.

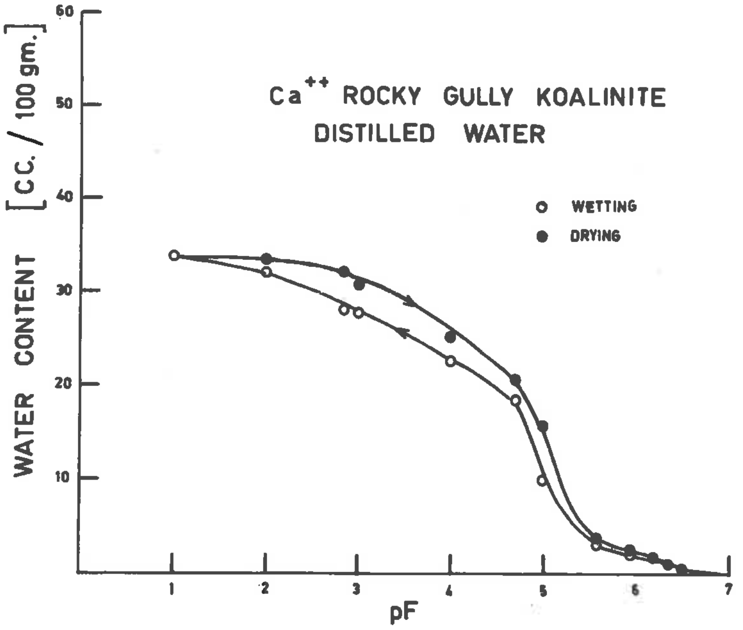


FIGURE 38.

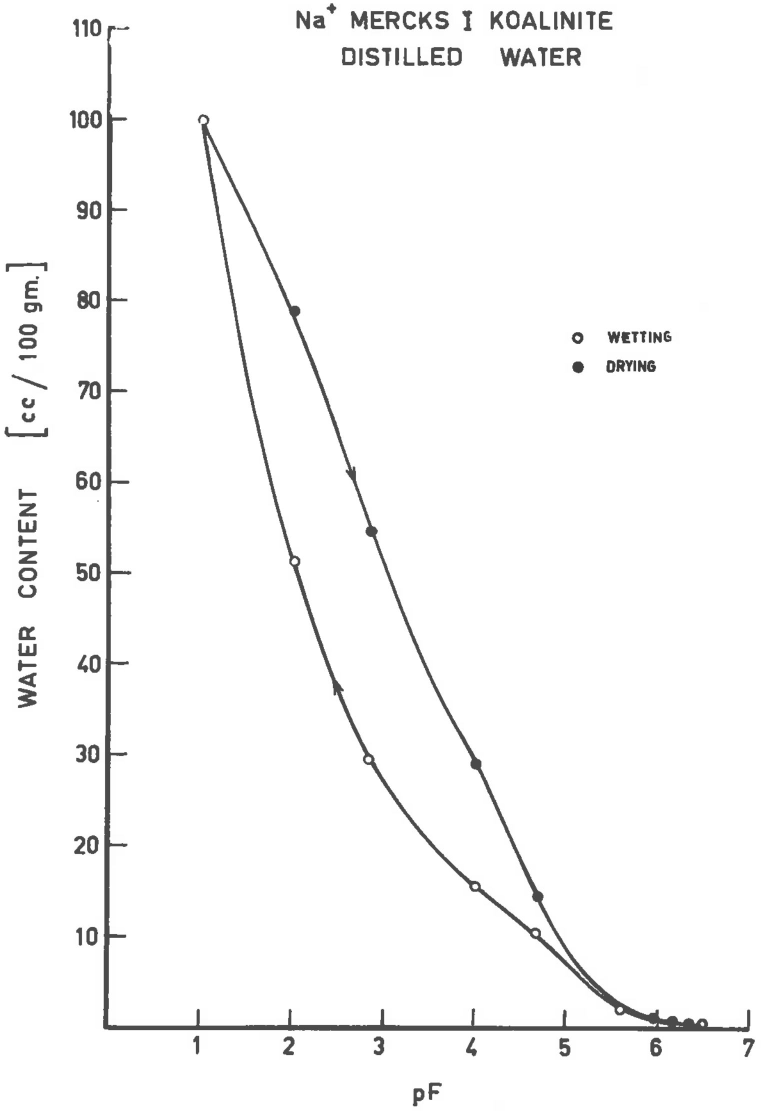


FIGURE 39.

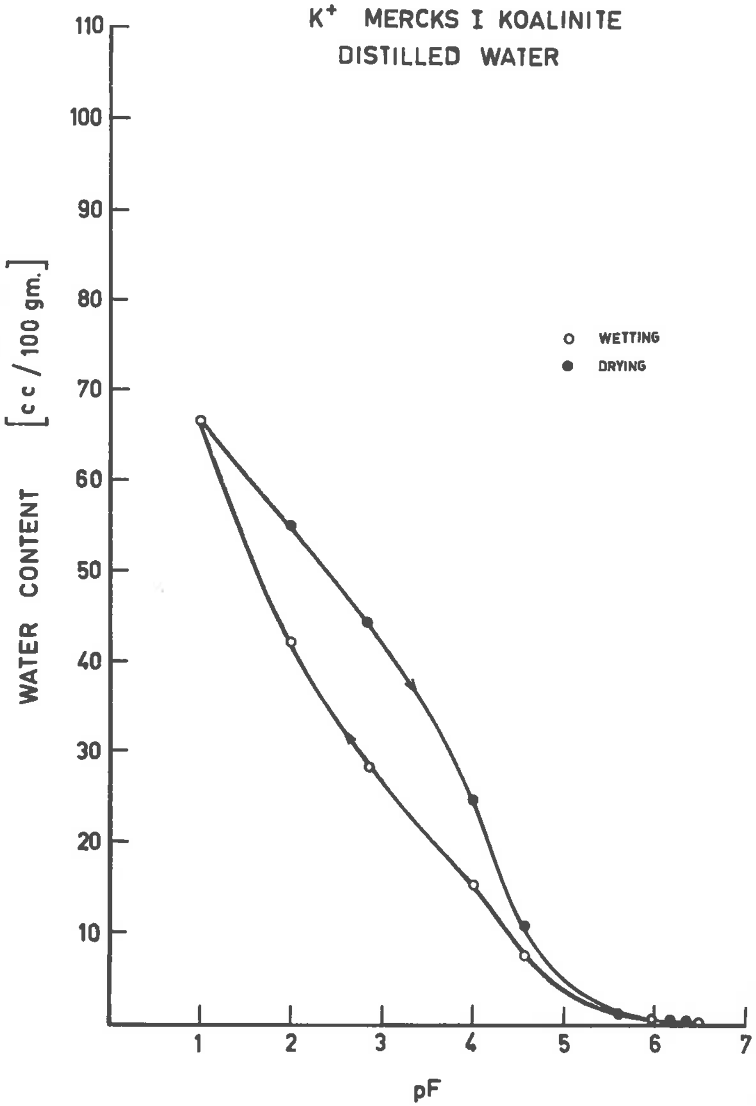


FIGURE 40.

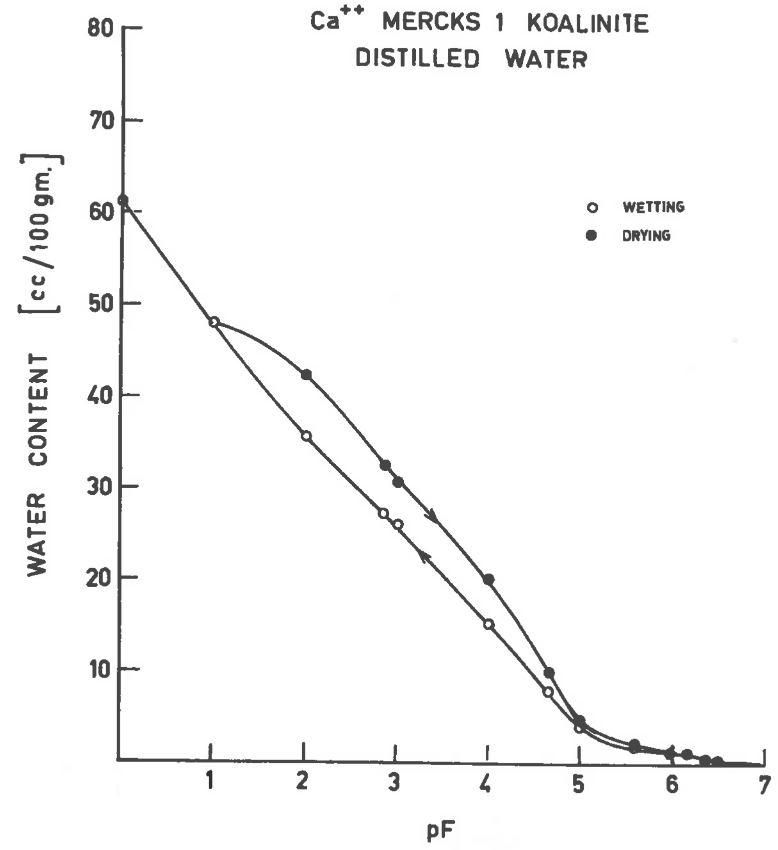


FIGURE 41.

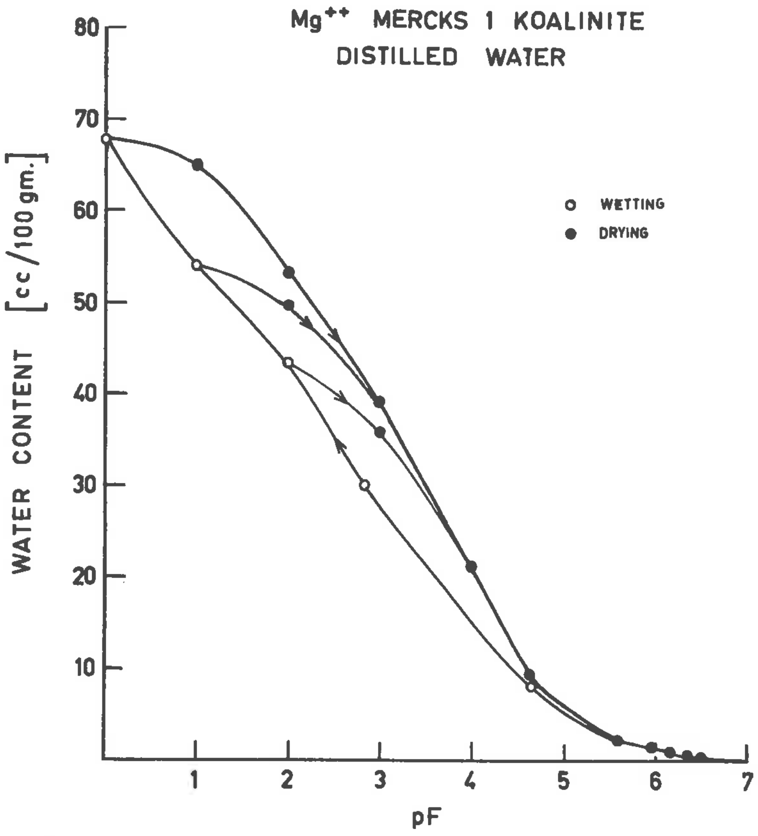


FIGURE 42.

evidence for the Mercks I cores.

Schofield and Samson (1954) have demonstrated the existence of strong positive edge to negative face attractions in kaolinite clays causing flocculation in salt free suspension. Deflocculation was found to be brought about in several ways :

(1) By proton transfer on addition of NaOH and consequent removal of positive charges.

(2) By anion adsorption, causing neutralization of positive charges and

(3) By small negatively charged platelets of another clay such as montmorillonite or illite overlying the positive charges on the edge faces of the larger kaolinite crystals.

Since the Mercks I kaolinite contains a small proportion of mica as an impurity and to determine whether the above forces were operative in restricting the swelling of the Rocky Gully kaolinite, a sample of the sodium clay was titrated with sufficient sodium tri-polyphosphate ($Na_5P_3O_{10}$) to cause deflocculation. The suspension was filtered, dried and cores made as before. On wetting to 100 cm suction similar water contents as those for the untreated clay were obtained.

The addition of 5 per cent and 10 per cent by weight of the $< 0.2\mu$ fraction of sodium Grundite illite to a suspension of Rocky Gully kaolinite was similarly ineffective producing only an increase in water content for the cores at 100 cm suction equivalent to that for the illite present. It can therefore be concluded that the observed restriction to swelling for the Rocky Gully kaolinite cannot be attributed to positive edge to negative face attractions.

The water contents at several pF values for a number of other kaolin materials were obtained and these are recorded in Table 7 in addition to the corresponding values for Rocky Gully and Mercks I kaolinites.

TABLE 7

WATER CONTENT FOR KAOLIN CORES ON WETTING TO VARIOUS pF VALUES

| Clay | Ion | Water Content (cc/100g) | | | | Specific surface area $m^2/g$ |
|---|---|---|---|---|---|---|
| | | pF | 2.84 | 2.0 | 1.0 | |
| Rocky Gully | $Na^+$ | | 28.4 | 33.0 | 35.5 | 36.3 |
| | $K^+$ | | 27.5 | 31.1 | 34.0 | |
| | $Ca^{++}$ | | 28.0 | 32.0 | 33.8 | |
| | $Mg^{++}$ | | 28.4 | 32.4 | 35.5 | |
| Mercks I | $Na^+$ | | 29.7 | 51.0 | 102 | 11.5 |
| | $K^+$ | | 28.3 | 42.2 | 66.8 | |
| | $Ca^{++}$ | | 27.0 | 35.5 | 48.0 | |
| | $Mg^{++}$ | | | 43.4 | 54.0 | |
| Mercks II | $Na^+$ | | | 25.4 | 27.8 | 11.2 |
| | $Ca^{++}$ | | 20.8 | 22.5 | 24.3 | |
| Malone | $Na^+$ | | 22.5 | 30.7 | 37.3 | 17.4 |
| | $Ca^{++}$ | | 23.4 | 26.3 | 28.3 | |
| Eureka Halloysite | $Na^+$ | | | 21.6 | 22.7 | 109.8 |
| | $Ca^{++}$ | | 18.1 | 19.2 | 20.5 | |
| New Zealand | $Na^+$ | | | 41.1 | 46.9 | 40.2 |
| | $Ca^{++}$ | | 32.8 | 35.7 | 39.6 | |

The variation that exists between the different kaolin minerals on wetting is obvious; the outstanding feature of the results being the apparent lack of correlation between water content at low pF values and factors such as specific surface area and exchangeable cation. The sharp contrast between the behaviour of Mercks I kaolinite and the remainder of the kaolins is illustrated by the water contents on wetting to pF 1 listed in column 5. It has the same specific surface area as Mercks II kaolinite yet takes up approximately four times as much water when sodium saturated. On the other hand Eureka Halloysite with approximately ten times the specific surface area of the Mercks kaolinites takes up less water than any of the other kaolins, barely exceeding the oven dry porosity value. The behaviour of the Malone and New Zealand kaolinites like that of Rocky Gully appears to be intermediate between the extremes typified by Eureka Halloysite and Mercks I kaolins.

Complete nitrogen adsorption-desorption isotherms were not obtained for these additional kaolinites. However, a general idea of the shape of the water vapour desorption isotherm and hence of the pore size distribution for the cores of these materials can be obtained from the water contents for the calcium clays at several relative vapour pressures listed in Table 8.

It can be seen that with the exception of Eureka Halloysite the desorption isotherms of the additional kaolinites are similar to those of Rocky Gully and Mercks I kaolins indicating the majority of the porosity in pores in excess of approximately 50 Å equivalent cylindrical radius. This point is discussed later in more detail.

The experimentally determined relationships between total volume and water content for Rocky Gully and Mercks I kaolinites are shown in Figures 43 and 44, respectively. The points plotted are those for the calcium saturated clays but within experimental error the curves are equally representative of the relationships obtained for the other cations. Although the variation between cores results in appreciable scatter for Rocky Gully kaolin it is apparent that for both clays normal shrinkage ceases at a value equal to the final porosity. Any further reduction in film thickness is accommodated within the rigid network formed by the large kaolinite crystals.

## TABLE 8

## WATER CONTENT OF KAOLINITE CORES ON DRYING TO VARIOUS RELATIVE VAPOUR PRESSURES

| | Water Content cc/100g | | | |
|---|---|---|---|---|
| Relative Vapour Pressure | 0.96 | 0.75 | 0.51 | Oven Dry Porosity (cc/100g.) |
| pF | 4.7 | 5.6 | 6.0 | |
| Equivalent Pore Radius | 262 | 38 | 15 | |
| Clay | | | | |
| Ca$^{++}$ Rocky Gully | 18.4 | 3.2 | 2.2 | 18.5 |
| Ca$^{++}$ Mercks I | 8.0 | 1.9 | 1.4 | 18.8 |
| Ca$^{++}$ Mercks II | 8.8 | 1.73 | 1.49 | 18.9 |
| Ca$^{++}$ Malone | 15.7 | 2.73 | 2.26 | 18.9 |
| Ca$^{++}$ Eureka | 17.1 | 11.6 | 9.3 | 18.9 |
| Ca$^{++}$ New Zealand | 25.1 | 2.92 | 2.49 | 25.9 |

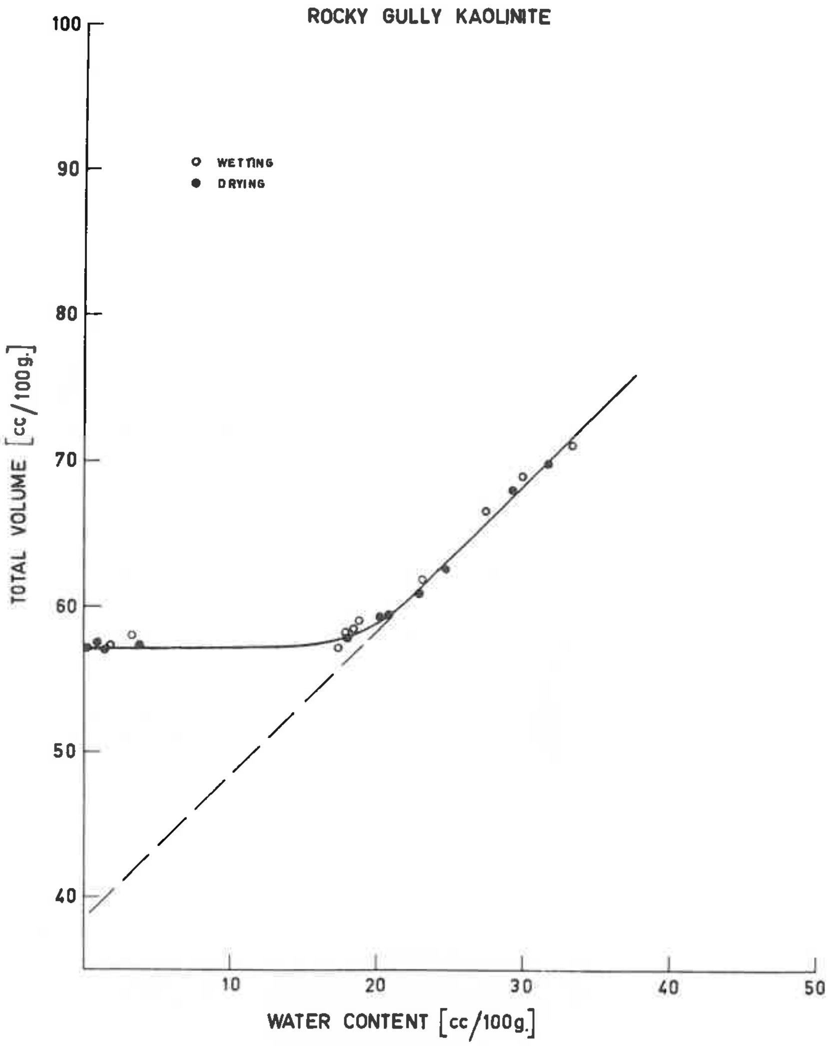


FIGURE 43.

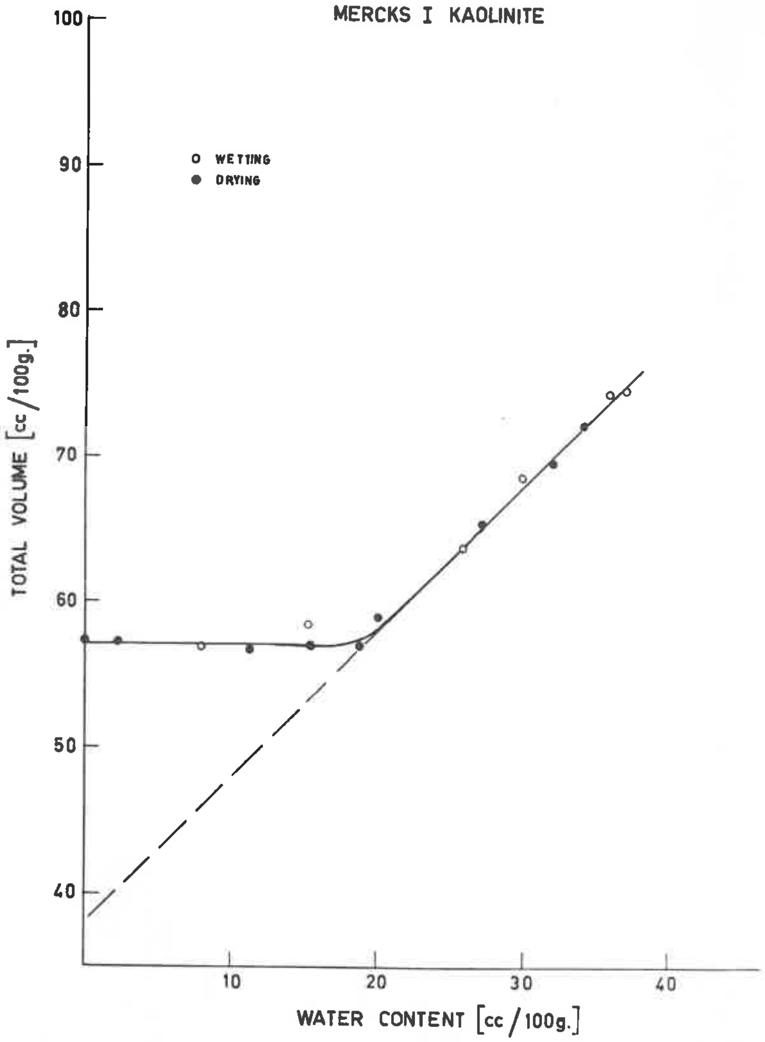


FIGURE 44.

### 2.1.2. Effect of electrolyte Concentration.

### Sodium Chloride.

The effect of increasing concentration of sodium chloride on the drying curve after wetting to pF 1 was determined for both the sodium saturated Rocky Gully and Mercks I kaolins. The drying curves for Rocky Gully for all the concentrations used were identical with that obtained for distilled water and are therefore not reproduced. The marked effect of increasing concentration of sodium chloride on the behaviour of Mercks I kaolin is shown in Figure 45. The distilled water drying curve is included for comparison.

In Table 9 the insensitivity of the remaining kaolinites to increasing concentrations of sodium chloride is illustrated by the solution contents at pF 1.

TABLE 9

EFFECT OF SODIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT OF KAOLINS ON WETTING TO pF 1

| | Solution Content (cc/100g) | | | | |
|---|---|---|---|---|---|
| Concentration | Distilled water | $\frac{N}{100}$ | $\frac{N}{10}$ | $\frac{N}{4}$ | N |
| Clay | | | | | |
| $Na^+$ Rocky Gully | 35.5 | 35.1 | 35.1 | 35.3 | 37.3 |
| $Na^+$ Mercks I | 102 | 77.7 | 69.5 | 59.5 | 49.4 |
| $Na^+$ Mercks II | 27.8 | 28.0 | 27.2 | 27.8 | 28.4 |
| $Na^+$ Malone | 37.3 | 36.5 | 35.5 | 35.1 | 34.3 |
| $Na^+$ New Zealand | 46.9 | 48.4 | 47.7 | 47.4 | 46.0 |
| $Na^+$ Eureka | 22.7 | 22.7 | 22.9 | 24.2 | 24.0 |

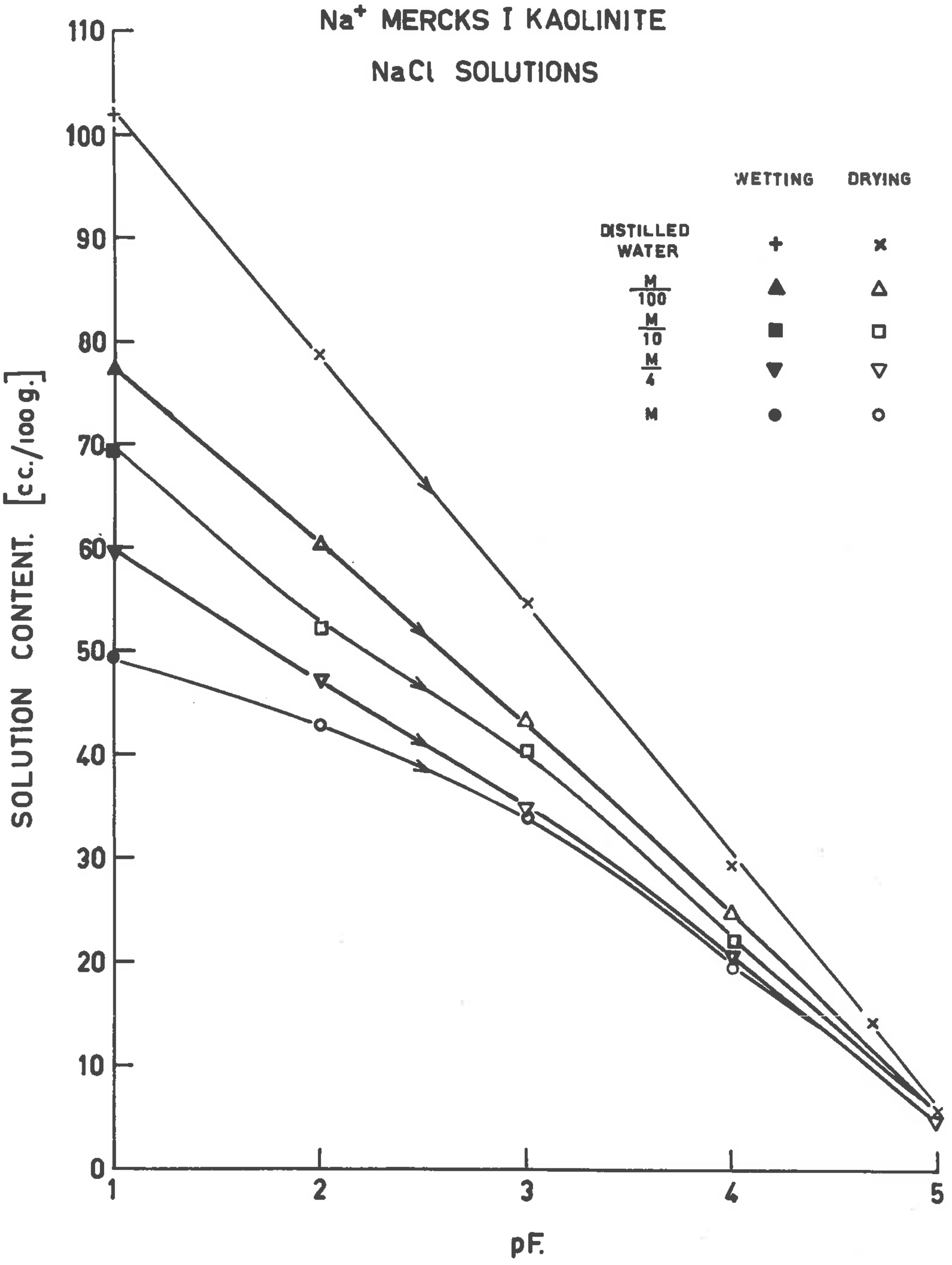

Na⁺ MERCKS I KAOLINITE
NaCl SOLUTIONS
WETTING
DRYING
DISTILLED WATER
M/100
M/10
M/4
M
SOLUTION CONTENT. [c.c./100 g.]
pF.
0
10
20
30
40
50
60
70
80
90
100
110
1
2
3
4
5

FIGURE 45.

## Calcium Chloride Solutions.

The drying curves after wetting to pF 1 with different concentrations of calcium chloride solution for calcium Rocky Gully and Mercks I kaolins are shown in Figures 46 and 47 respectively. Rocky Gully kaolin shows the anomolous behaviour of a slight increase in volume of solution taken up with increasing concentration. This increase is accompanied by a slightly more plastic and sticky texture for the clay cores. Mercks I whilst showing little significant variation in volume taken up between distilled water and molar calcium chloride, shows an appreciable restriction in swelling in four molar calcium chloride solution.

The remainder of the kaolinites behave in a similar manner to Rocky Gully showing varying increases in volume of solution taken up with increasing concentration at pF 1 (Table 10).

TABLE 10

EFFECT OF CALCIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT OF KAOLINITES ON WETTING TO pF 1

| | Solution Content (cc/100g) | | | | |
|---|---|---|---|---|---|
| Concentration | Distilled water | $\frac{M}{100}$ | $\frac{M}{10}$ | M | 4M |
| Clay | | | | | |
| $Ca^{++}$ Rocky Gully | 33.8 | 33.8 | 34.9 | 36.2 | 38.6 |
| $Ca^{++}$ Mercks I | 48.0 | 46.4 | 47.4 | 47.5 | 41.7 |
| $Ca^{++}$ Mercks II | 24.3 | 23.9 | 23.3 | 24.8 | 25.2 |
| $Ca^{++}$ Malone | 28.3 | 29.1 | 29.4 | 31.7 | 33.3 |
| $Ca^{++}$ New Zealand | 39.6 | 40.7 | 41.3 | 42.7 | 45.6 |
| $Ca^{++}$ Eureka | 20.5 | 21.3 | 21.5 | 22.5 | 23.0 |

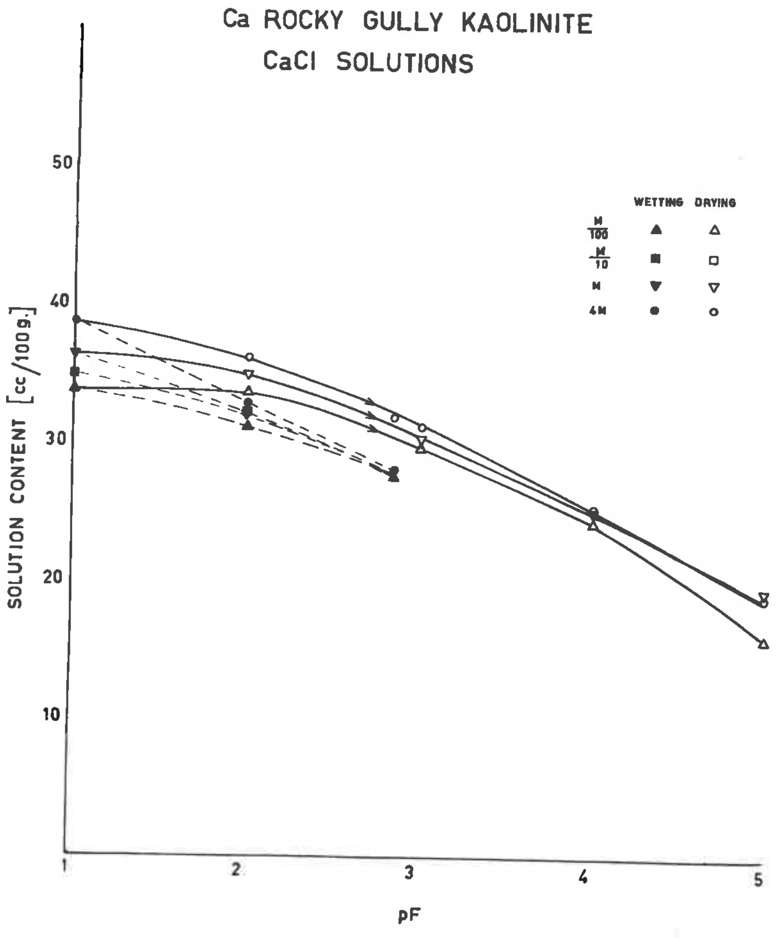


FIGURE 46.

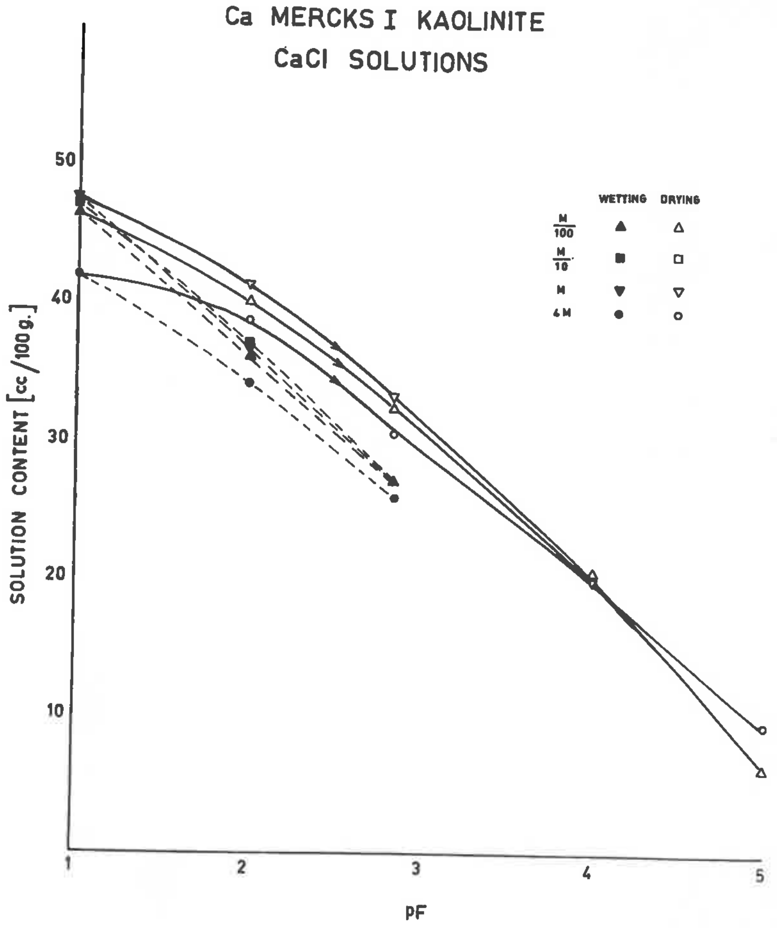


FIGURE 47.

### 2.1.3. Discussion.

Although the kaolin minerals have generally been regarded as non-swelling it is apparent that appreciable swelling does occur and that wide variations in behaviour are possible. In this regard the behaviour of the kaolins studied may be divided into three categories.

Eureka halloysite shows almost negligible swelling and in view of its large specific surface area and consequent small particle size, the rigidity of this material even when saturated with monovalent ions indicates the existence of very strong attractive forces between individual clay particles.

Into a second category may be grouped the remainder of the kaolins with the exception of Marcks I kaolinite. These clays do exhibit a limited amount of swelling with varying small dependence on the exchangeable cation present.

For these two categories there is no indication of any increase in solution uptake for either monovalent or divalent systems with decreasing electrolyte concentration as would be expected from diffuse double layer considerations.

Marcks I kaolinite provides the third category in which considerable swelling occurs and the concentration of electrolyte present has a significant effect on solution uptake although in the divalent ion case this effect is not as large as might be expected.

Since there is little correlation between swelling and specific surface area it would seem that the total absorption of solutions by these materials is determined almost entirely by the structural strength of the system rather than by the physico-chemical development of diffuse double layers on the clay surfaces.

In the case of Eureka halloysite one possible source of the strong short range attractive forces is hydrogen bonding between the close packed hydroxyl sheet of the octahedral layer of one crystal and the open packed oxygen network of the tetrahedral layer of an adjacent crystal. Such forces have been suggested as responsible for the restriction of the interlamellar spacing of an hydrated halloysite to one layer of water molecules. If as seems probable the halloysite crystals are oriented into parallel groups or domains on drying or compression a similar restriction to one layer of water molecules between crystals seems possible and could account for the negligible swelling of this material. This suggestion is clearly not tenable since the surface area of the halloysite crystals is readily measured by nitrogen adsorption so that minimum separations approaching 10 Å would be expected. It is possible however, that this general parallel arrangement could exist and that there are small areas where closer contact is achieved and the restricted swelling may be the result of a number of hydrogen bonds in these areas of close contact.

The interpretation of the solution content-energy data for the remaining kaolin materials in terms of film thickness developed on the clay surface and hence the applicability of diffuse double layer considerations is very dependant on the manner in which the pore size distribution is assumed to arise. The pore size distributions obtained for Rocky Gully and Mercks I kaolinites by nitrogen desorption, and the water vapour desorption points for the additional kaolinites, indicate that more than three quarters of the total porosity of the kaolinite cores arises from pores in excess of about 50 Å equivalent cylindrical radius. As pointed out in Section 2 surface separations of up to 100 Å or more could easily arise from steps in crystal faces between parallel crystals for such large crystals as well as between randomly arranged crystals and because of the relatively small specific surface areas of the kaolinites the degree of orientation into domains is difficult to ascertain.

Consequently the relatively small swelling and independence of electrolyte concentration exhibited by the kaolinites of the intermediate category could be interpreted in a number of ways.

If a relatively large proportion of the surface area is accommodated in steps between oriented crystals it is possible that considerable development of diffuse double layers could occur without much resultant swelling pressure within the clay mass.

Alternatively if the surfaces of the crystals are not appreciably stepped the absence of appreciable external swelling could be brought about by internal accommodation of the swelling between parallel plates within the large pores between adjacent domains. With crystals as large as those for the kaolinites this possibility does, however, seem unlikely.

A similiar lack of swelling pressure in spite of the development of diffuse double layers could equally well arise from their accommodation within a network of the large kaolinite crystals randomly placed (unstacked) and only in contact at relatively few points as in Figure 32(b).

In actual fact all three structural factors may contribute to a non-dependance of swelling on surface film thickness. In each case large variations in film thickness with electrolyte concentration could occur without affecting total solution uptake since the porous structure could retain solution by capillary action.

From this it is apparent that either of the methods of calculation proposed in Section 3 could be equally correct in giving an estimate of the film thickness regardless of the nature of the structural configuration whether highly oriented or not. However, in the absence of any complicating restrictions the values for film thickness obtained by dividing total solution content by specific surface area should at least equal that predicted by diffuse double layer theory if diffuse double layers are developed on the clay surfaces.

In Table 11 the water film thickness on the clay surfaces for the kaolins on wetting to pF 1 with distilled water has been calculated by both procedures (Section 3).

The theoretical value of film thickness for a concentration of monovalent ions of $10^{-4}$ molar at pF 1 is 400 Å. Hence it is apparent that with the exception of Mercks I kaolinite the maximum film thickness possible in distilled water is much less than that predicted by diffuse double layer theory indicating that additional restrictions to swelling are operative.

If, on the other hand, the clay crystals are considered as well oriented into parallel positions with the majority of the porosity arising between domains the values obtained by application of swelling pore theory may provide better estimates of the actual film thickness. In this

## TABLE 11

## CALCULATED FILM THICKNESS FOR KAOLINS ON WETTING TO pF 1 ON DISTILLED WATER

| Method of Calculation | | Calculated Film Thickness (Å) | | Surface Density of Charge x $10^{-7}$ me/cm$^2$ |
|---|---|---|---|---|
| | | Total Water Content / Specific Surface Area | Swelling Pore Theory | |
| Clay | Cation | | | |
| Rocky Gully | $Na^+$ | 98 | 29 | 1.1 |
| Kaolinite | $K^+$ | 95 | 27 | |
| | $Ca^{++}$ | 93 | 26 | 1.7 |
| | $Mg^{++}$ | 98 | 29 | |
| Mercks I | $Na^{++}$ | 887 | 474 | 6.1 |
| Kaolinite | $K^+$ | 581 | 272 | |
| | $Ca^{++}$ | 418 | 163 | |
| | $Mg^{++}$ | 470 | 198 | |
| Mercks II | $Na^{++}$ | 248 | 48 | 1.8 |
| Kaolinite | $Ca^{++}$ | 217 | 28 | |
| Malone | $Na^{++}$ | 214 | 71 | 2.5 |
| Kaolinite | $Ca^{++}$ | 163 | 37 | |
| Eureka | $Na^+$ | 21 | 2.7 | 0.7 |
| Halloysite | $Ca^{++}$ | 19 | 1.4 | |
| New Zealand | $Na^+$ | 117 | 22 | 0.8 |
| Kaolinite | $Ca^{++}$ | 99 | 12 | |

case it is apparent that the film thicknesses for all but Mercks I kaolin are not at all compatible with diffuse double layer theory.

It is interesting to note however that the water film thicknesses calculated on this basis for the sodium clays do bear some relation to the surface density of change for the respective clay minerals.

increasing surface density of change is coupled with increasing water film thickness. In fact, for the clays in the intermediate category the relationship between calculated film thickness and surface density of change is linear (Figure 48).

Since positive edge to negative face attraction does not appear to be significantly operative in restricting swelling some other origin for interparticle bonding or attractions is indicated for these materials. One possibility arises from the suggestion by Cashen (1959) that as the kaolinite clays are washed free of electrolyte the crystals become unstable due to a rise in potential difference between negative planar and positive edge faces allowing the migration of edge face aluminium ions to exchange sites on the planar faces. Thus by the present method of preparation the swelling of the kaolinite clays could possibly be dominated by the presence of aluminium ions. However, if this is the case it is difficult to see why the Mercks I kaolinite is not equally as restricted as Mercks II kaolinite. In addition the treatment of sodium Rocky Gully kaolinite with sodium tripolyphosphate should nullify the effect of aluminium on planar faces and prevent further migration from the edge faces as shown by Cashen with pyrophosphate.

The possibility of hydrogen bonding between the silica and gibbsite sheets of adjacent crystals as suggested earlier for Eureka halloysite is once again a likely source of restriction to swelling. The number of such hydrogen bonds could determine the force necessary to cause appreciable swelling in much the same fasion as the swelling of exchange resins is determined by the number of cross-linkages present (Dowex, 1958). Clearly at close distances of approach electrostatic

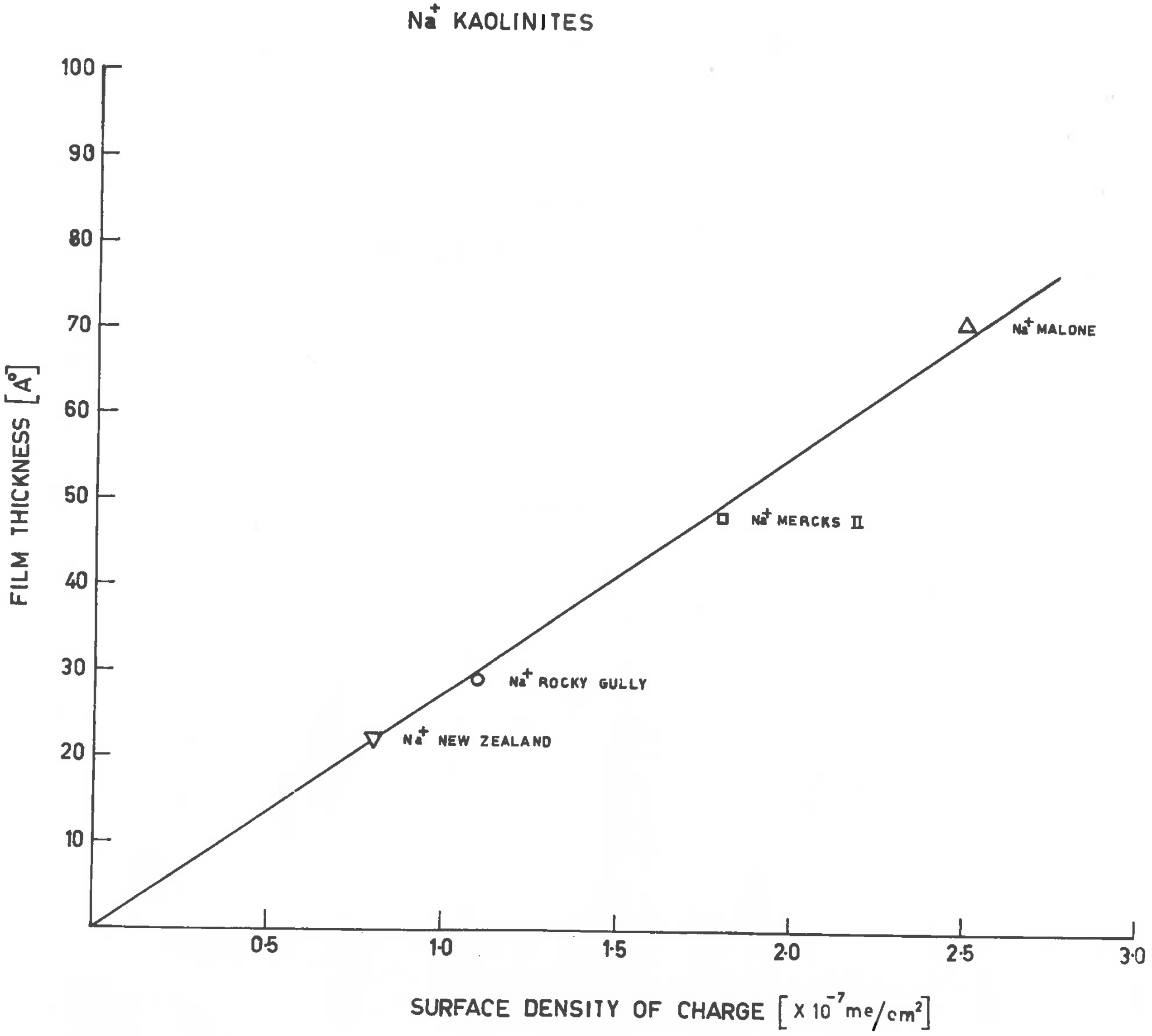

Na+ KAOLINITES
FILM THICKNESS [A°]
100
90
80
70
60
50
40
30
20
10
0·5
1·0
1·5
2·0
2·5
3·0
SURFACE DENSITY OF CHARGE [x 10-7 me/cm2]
Na+ MALONE
Na+ MERCKS II
Na+ ROCKY GULLY
Na+ NEW ZEALAND

FIGURE 48.

forces would also be involved and here the region of dielectric saturation associated with the exchangeable cations would exert an influence. This latter consideration could possibly explain the difference in swelling of the monovalent and divalent ion kaolinites grouped into the intermediate category.

The inertia and frictional resistance to movement of the large kaolinite crystals may also provide an additional hinderance to swelling forces.

The repulsive force opposing the short range attractive forces would be the hydration energy of the exchangeable cations and the effectiveness of this repulsion would be determined largely by the surface density of charge possibly giving rise to the increase in swelling observed with increasing surface density of charge for the sodium clays.

If the surface density of charge is sufficiently large the hydration energy of the exchangeable cations may be sufficient to overcome the short range attractive forces allowing the full development of the water film on the clay surfaces. This may be the case for Mercks I kaolinite.

In Figure 49 the variation in film thickness with sodium chloride concentration and increasing suction after wetting to pF 1 for sodium Mercks I kaolinite calculated by both methods has been plotted in comparison with the theoretical film thickness on the basis of diffuse double layer theory. The points obtained by dividing solution contents by the specific surface area are obviously far in excess of diffuse double layer theory with the film thickness on wetting to pF 1 in molar sodium chloride solution being larger than that predicted for $10^{-4}$ molar

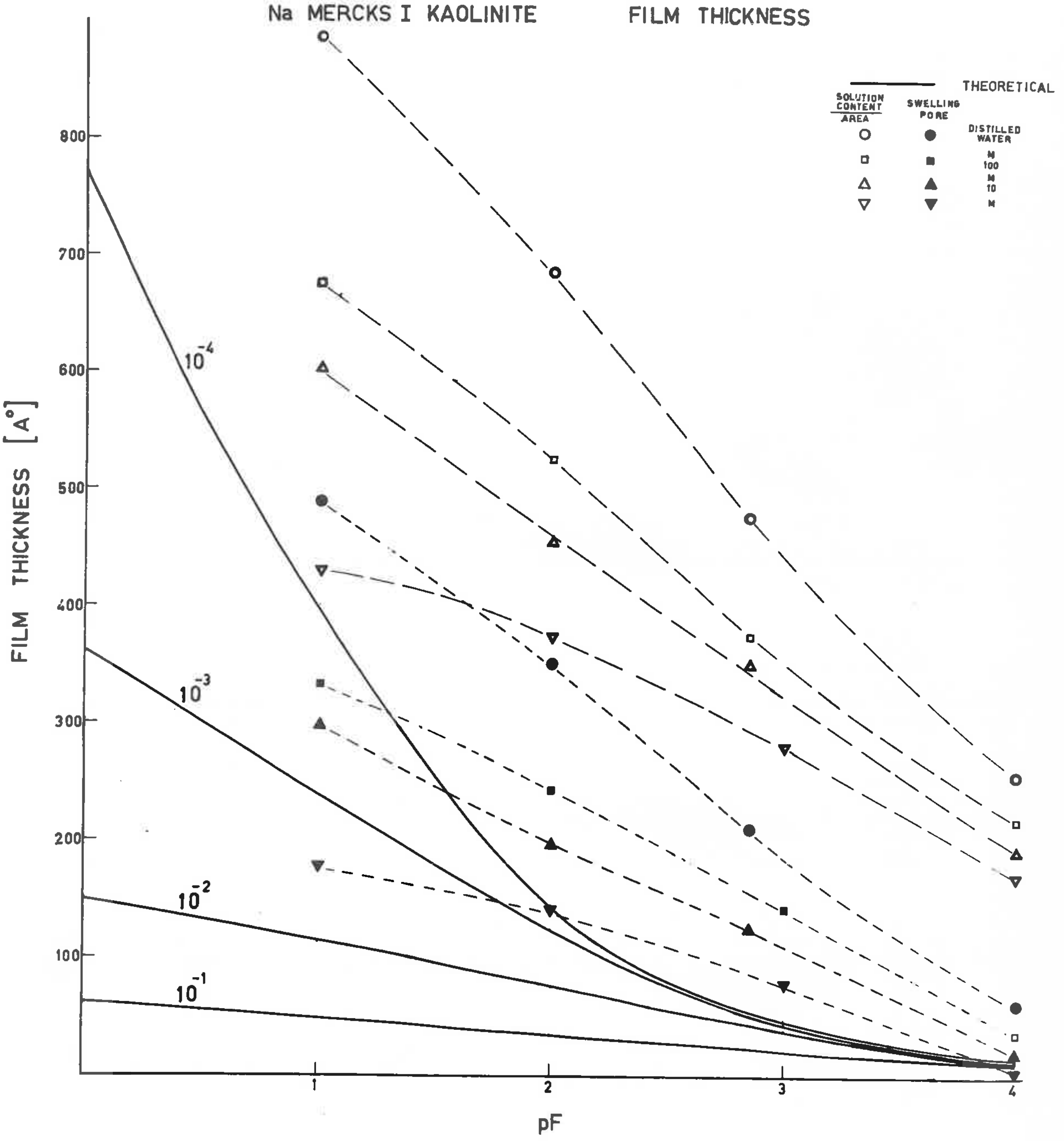

Na MERCKS I KAOLINITE
FILM THICKNESS
THEORETICAL
SOLUTION CONTENT / AREA
SWELLING PORE
DISTILLED WATER
M/100
M/10
M
FILM THICKNESS [A°]
800
700
600
500
400
300
200
100
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
1
2
3
4
pF

FIGURE 49.

sodium chloride solution. Subtraction of a proportionately swollen oven dry porosity from the solution contents whilst reducing the magnitude of the calculated film thicknesses provides no real agreement between theoretical and calculated values. For a monovalent kaolin after correction for positive adsorption on edge faces Quirk (1957) has obtained good agreement between measured chloride exclusion in suspension and that predicted by Schofield's(1947) negative adsorption theory indicating that diffuse double layers are formed for these systems. Hence the distribution of the points for the various concentrations in Figure 49 clearly indicates that the formation of an extensive gel structure enables the clay mass to enmesh a considerable amount more solution than is surface retained thereby masking to some extent the effect of electrolyte concentration on the diffuse double layer.

Similarly the negligible dependance of the swelling of the calcium Mercks I kaolinite on electrolyte concentration for concentrations less than molar could equally well be attributed to the gel formation.

Osmotic and hydrostatic components of free energy do not appear to be equivalent, the latter being far more effective in reducing the swelling of the sodium Mercks I clay. This again may be due to the presence of the gel structure since an increase in hydrostatic force on the gel structure could collapse it more effectively than a change in electrolyte concentration which does not apply as an actual force on the pore water.

## 2.2 Illites.

### 2.2.1. Distilled Water.

The water content-suction relationships obtained for Grundite and Willalooka illites when saturated with various cations are shown in Figures 50 to 53 and 54 to 57 respectively. Both clays show a marked variation in behaviour with valency of the exchangeable cation present but the dependence in the case of Willalooka illite is particularly dramatic. At water suctions below 100 cm the sodium saturated cores of this clay and to a lesser extent the potassium saturated, become fluid and collapse. This collapse is accompanied by the disappearance of hysteresis from the water content-energy relationship. At these values of pF the water content changes rapidly with applied suction.

When saturated with divalent calcium or magnesium ions the Willalooka illite cores remain quite rigid and exhibit comparatively little swelling the magnitude of which changes little with increase in pF from 0 to 4.

A similar though less extreme variation in behaviour with valency of the exchangeable cation is shown by the Grundite illite. The swelling of the divalent clay although restricted, shows a greater dependence on applied suction than is the case for Willalooka illite. The monovalent cores do not, however, collapse even at zero tension. It is interesting to note the similarity in the water content of the two clays when saturated with divalent ions compared with the large differences observed in the monovalent clays. On wetting to pF 1 both calcium clays have a water content of approximately 45 cc/100g whilst at the same suction sodium Willalooka has a water content of 841 cc/100g

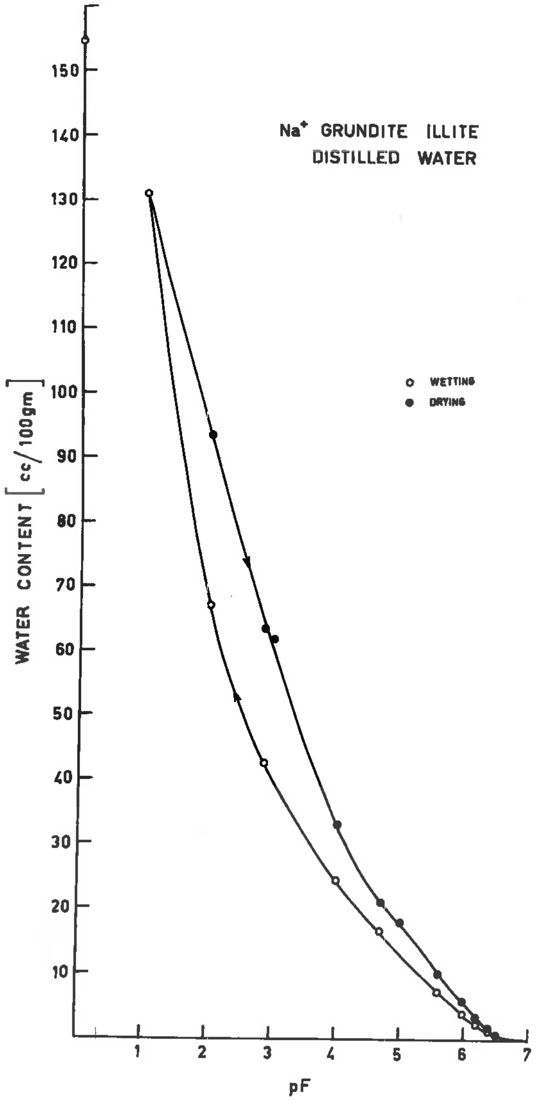


FIGURE 50.

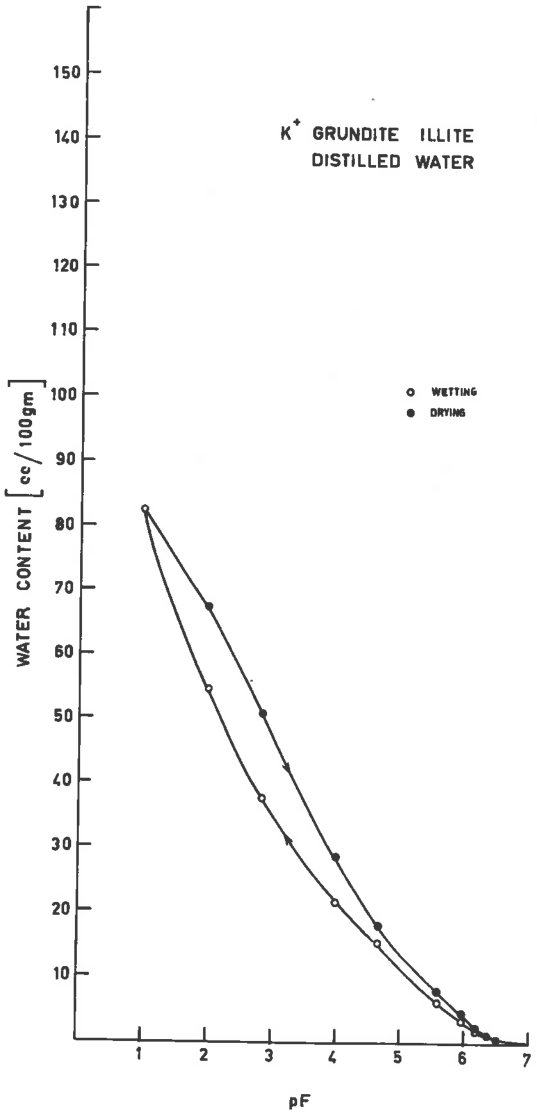


FIGURE 51.

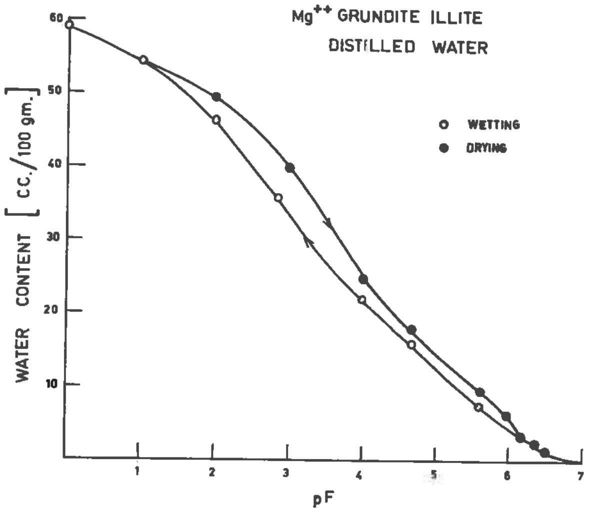


FIGURE 53.

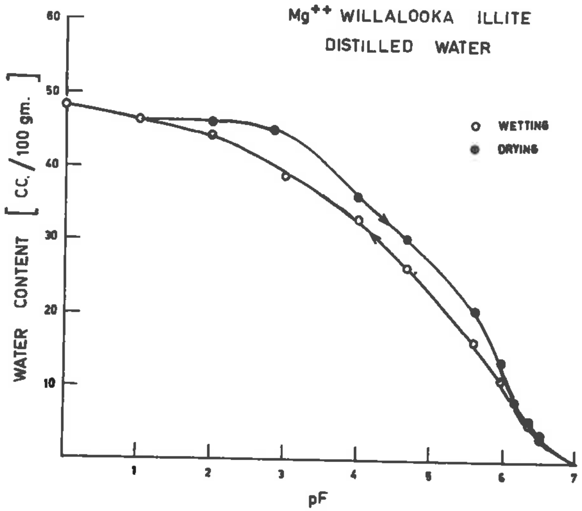


FIGURE 55.

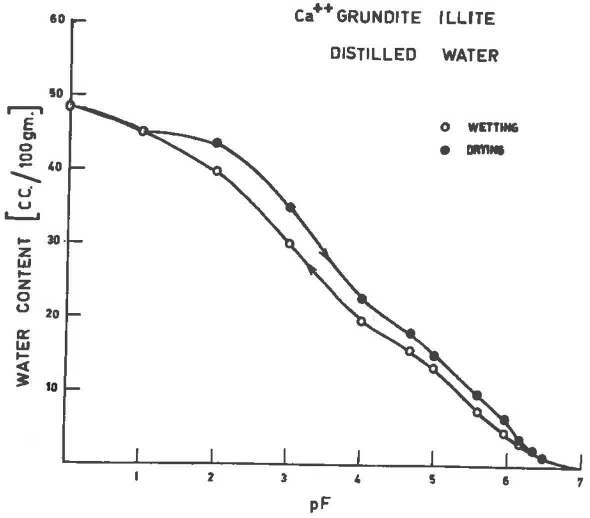


FIGURE 52.

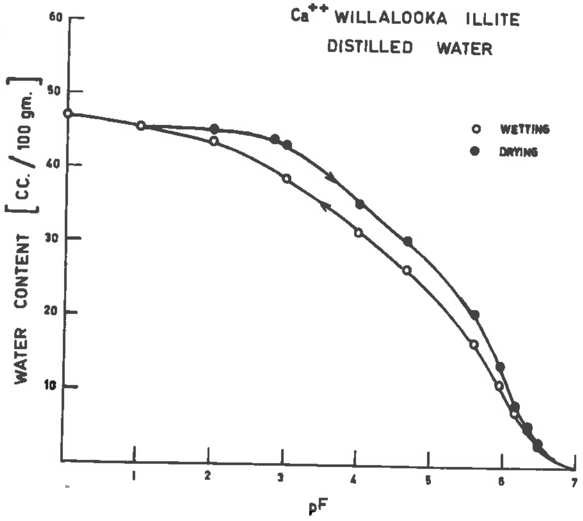


FIGURE 54.

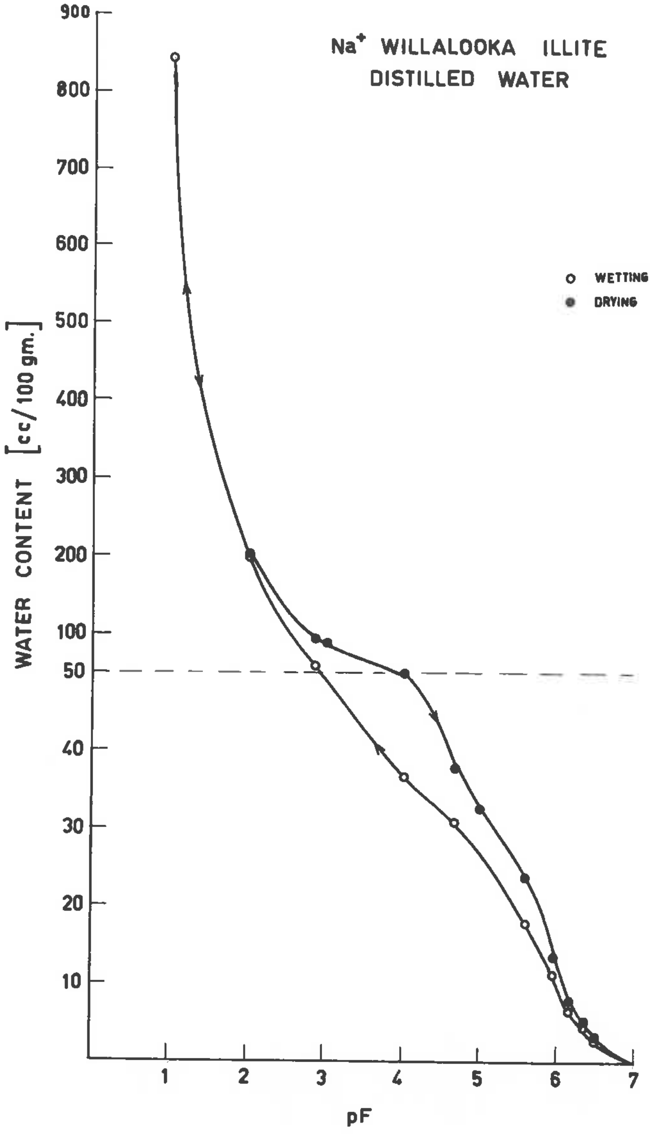


FIGURE 56.

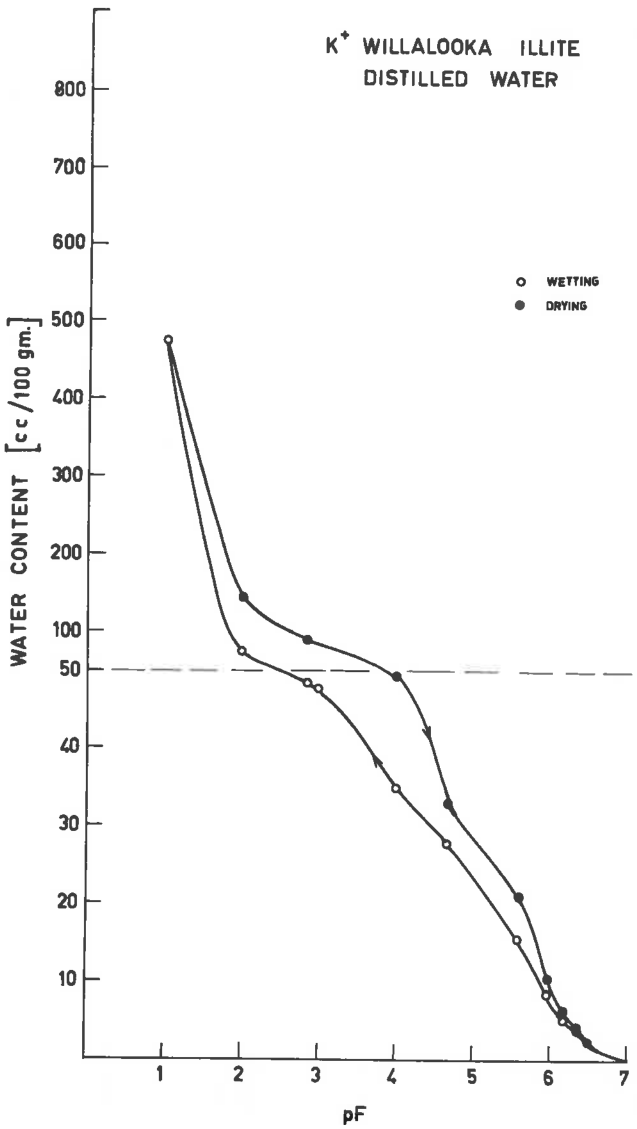


FIGURE 57.

compared with 130 cc/100g for the sodium Grundite illite.

In view of the much greater specific surface area of the Willalooka illite it is obvious that when saturated with divalent ions the swelling of this clay is subjected to a far greater restriction than is the case for the Grundite clay. The possibility of the presence of unexchanged aluminium ions causing this restriction was examined by washing the clay several times with molar calcium chloride plus $10^{-3}$ N HCl during the saturation process. The clay so treated gave identical results as those obtained for the untreated clay.

As an additional check on the nature of this restriction, its reversibility after sodium saturating was examined by resaturating a sample of the self-dispersing sodium clay using molar calcium chloride. The cores of this clay showed the same restricted swelling as the original calcium saturated clay.

From these results it can be inferred that this restriction is not one due to the presence of inorganic cements but is probably associated with the nature of the electrostatic attractive forces between adjacent particles.

It is worth noting at this point that the water-content-suction relationships obtained by Holmes (1955) for natural (divalent) Urrbrae B clay cores are very similar to those obtained for the divalent Willalooka cores in the present work. From the nitrogen studies in Section 2 these two clays appear to have similar structural configurations for the dry clay matrix; the difference in their behaviour from that of the Grundite illite may therefore be associated with the nature of this structural configuration.

It can be seen that for the monovalent Willalooka cores there appears to be a slight tendency for the wetting curves to flatten between pF 3 and 4 before the major swelling occurs and this suggests the presence of a potential barrier at this point. The potassium clay appears to be less capable of exceeding this barrier and the degree of swelling is reduced in comparison with that for the sodium clay. There is no indication of an equivalent flattening for the monovalent Grundite clays but the degree of swelling for the potassium clay is once again reduced in comparison with that for the sodium clay.

In the drying curves for the monovalent Willalooka clay the influence of exchangeable cation whether potassium or sodium is insignificant for pF values greater than 3 and the curves are similar indicating that the formation of a structural configuration may exert more control than the nature of the exchangeable cation.

In Table 12 the water content obtained on drying suspensions of the calcium clays in distilled water to several values of pF are shown.

TABLE 12

WATER CONTENT ON DRYING CALCIUM ILLITES FROM SUSPENSION

Water Content (cc/100g)

| Clay | Ca$^{++}$ Grundite Illite | Ca$^{++}$ Willalooka Illite |
|---|---|---|
| pF | | |
| 1 | 123 | 188 |
| 2 | 84.9 | 92.6 |
| 4 | 27.7 | 38.1 |

At low pF values a considerable amount more water is retained by the gel structures formed than by the cores but this is rapidly reduced by increasing hydrostatic suction and the water contents at pF 4 are similar to the drying values obtained for the calcium cores.

Figures 58 and 59 show the experimentally determined relationship between total volume and water content for the Grundite and Willalooka illite cores respectively. The points plotted are those for the calcium saturated clays but the points for the other cations lie essentially on the same line within experimental error. For both clays air appears to enter the system at a water content value just in excess of the oven dry porosity indicating that shrinkage is virtually complete at this point. Both wetting and drying points lie on the same line within experimental limits in agreement with the conclusions that hysteresis arises from plastic readjustments of particles with respect to each other and not from entrapped air giving variations in degree of saturation.

### 2.2.2. Effect of Electrolyte Concentration.

### Sodium Chloride Solutions.

The effect of concentration of sodium chloride solution on the drying curves of the sodium saturated Grundite and Willalooka illites after wetting to pF 1 are shown in Figures 60 and 61 respectively. The distilled water curves are included for comparison. Although there is a continuous reduction in swelling for both clays with increasing concentration of sodium chloride as would be expected from diffuse double layer considerations, the effect is obviously far greater for the Willalooka illite than for the Grundite illite. At pF 1 the solution

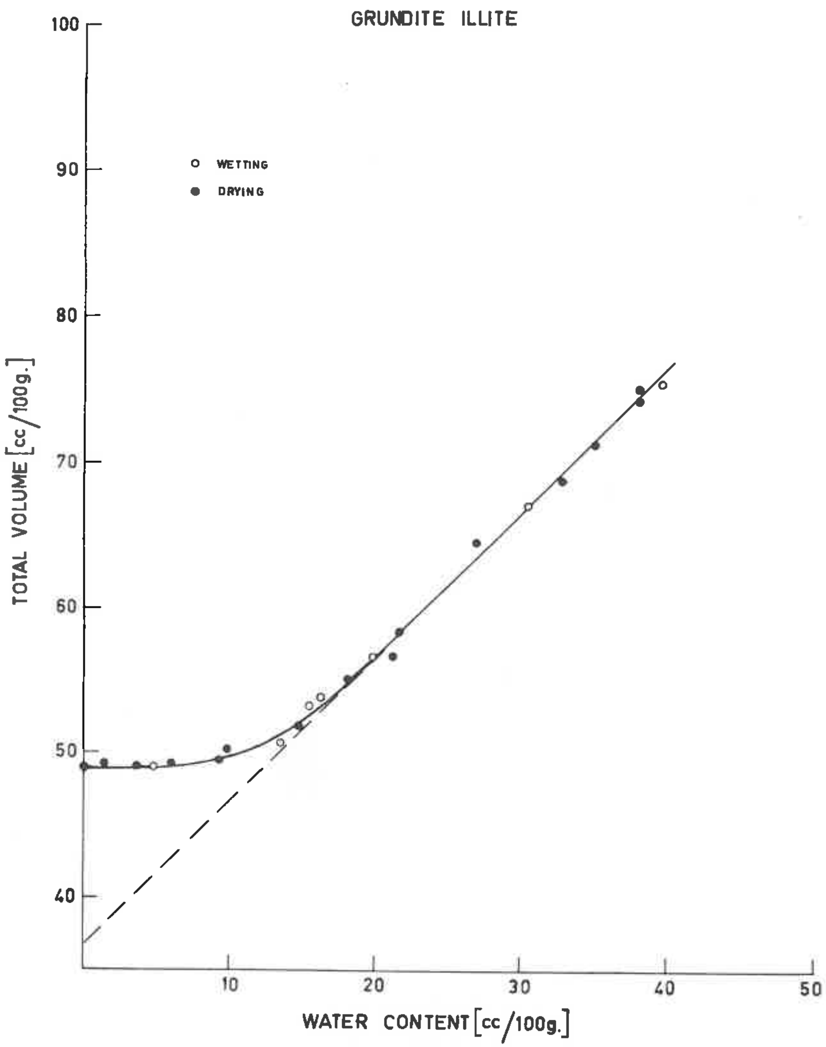


FIGURE 58.

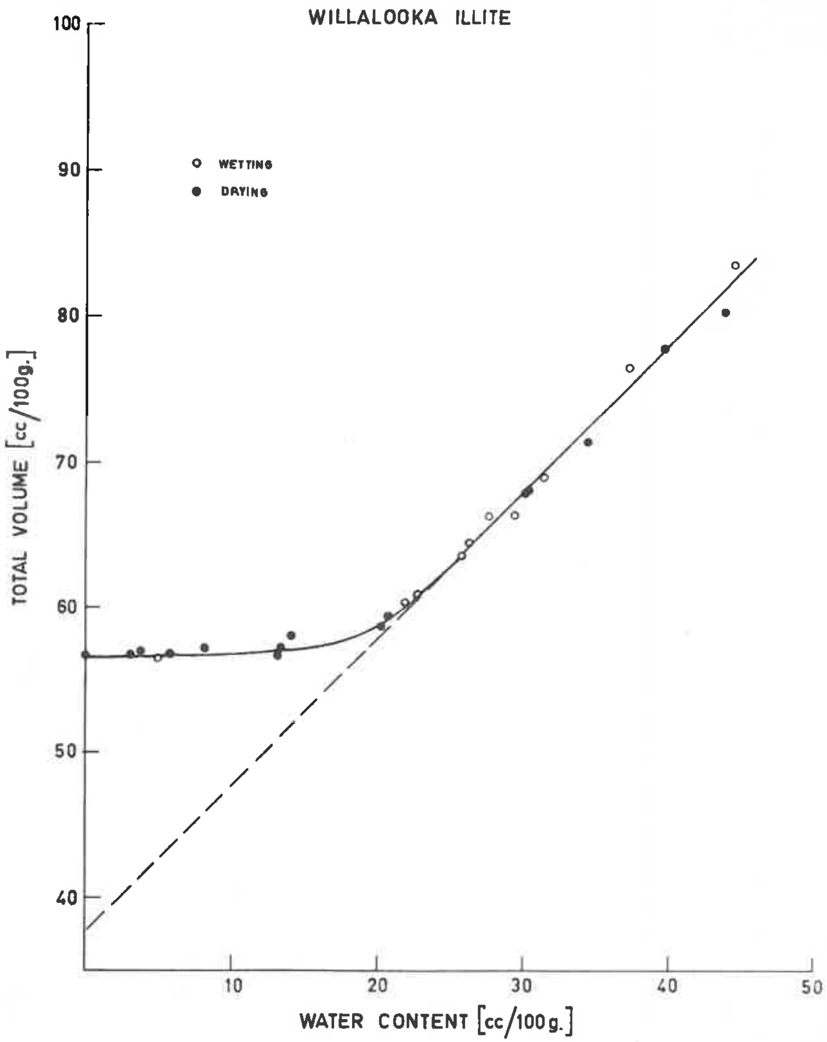


FIGURE 59.

uptake for Willalooka illite is reduced from 84.1 cc/100g for distilled water to 48.2 cc/100g for normal sodium chloride solution whereas that for Grundite illite is reduced from 131 cc/100g for distilled water to 57.5 cc/100g for normal sodium chloride. The drying curves for the stronger (N and $\frac{N}{4}$) sodium chloride solution concentrations for Willalooka illite are similar to those for the divalent calcium and magnesium clays in distilled water, showing very restricted swelling the magnitude of which changes comparatively little with increasing values of pF from 1 to 4. The swelling of the Grundite illite although restricted by the higher concentrations shows a greater dependence on applied suction at these concentrations.

The effect of concentration of sodium chloride on the solution content on drying to pF 1 from the suspension state for sodium Grundite and Willalooka illites is shown in Table 13. Suspensions of the sodium clays in distilled water were adjusted to the required concentrations by the addition of 2 M sodium chloride solution and then dried to pF 1 in perspex rings in the pressure plate apparatus.

TABLE 13

EFFECT OF SODIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON DRYING SUSPENSIONS TO pF 1

| | Solution Content pF 1 (cc/100g) | | | |
|---|---|---|---|---|
| Concentration | $\frac{N}{100}$ | $\frac{N}{10}$ | $\frac{N}{4}$ | N |
| Clay | | | | |
| $Na^+$ Grundite Illite | 252 | 246 | 219 | 189 |
| $Na^{++}$ Willalooka Illite | 216 | 282 | 309 | 377 |

Although the sodium Grundite gel shows an appreciable reduction

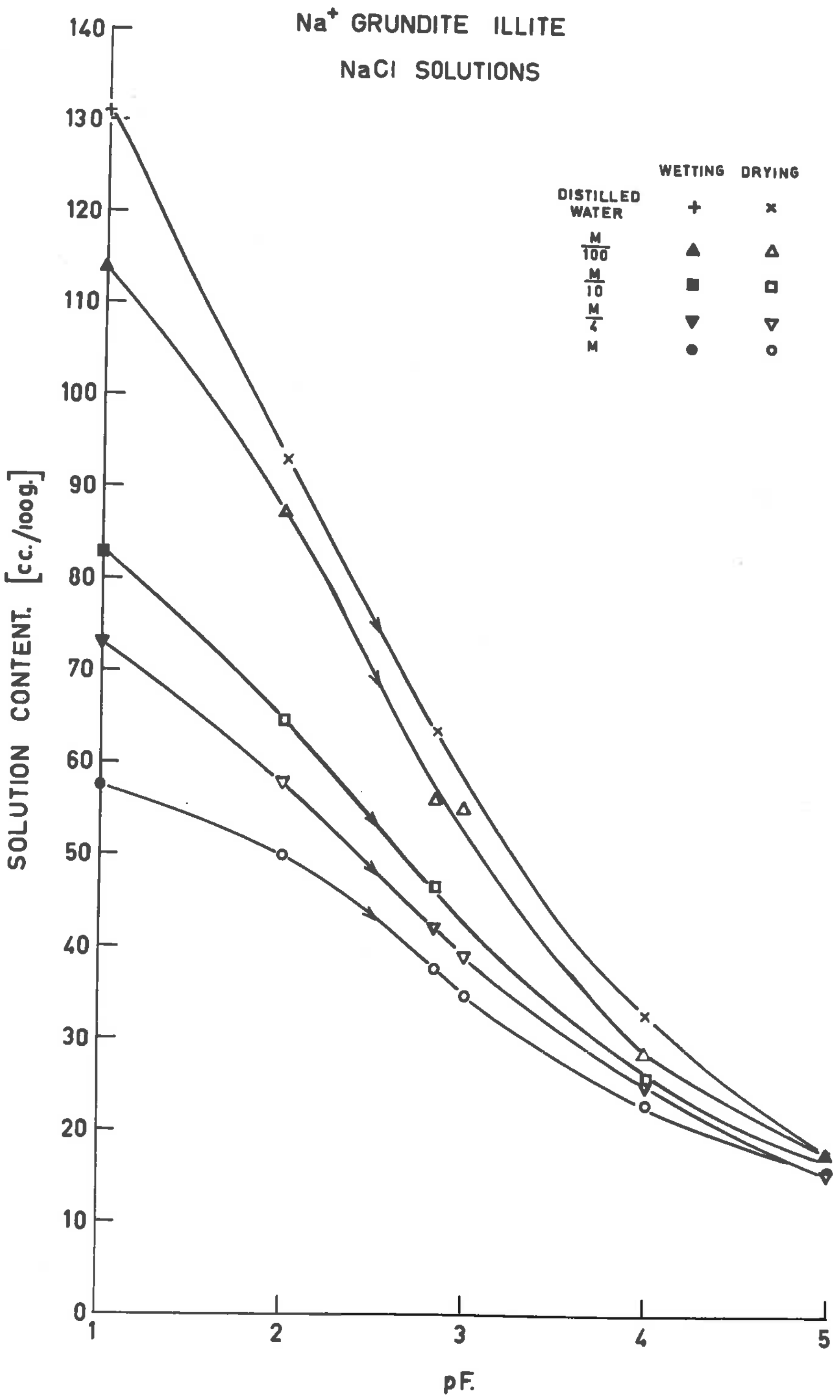

Na$^+$ GRUNDITE ILLITE
NaCl SOLUTIONS
WETTING
DRYING
DISTILLED WATER
+
×
M/100
▲
△
M/10
■
□
M/4
▼
▽
M
●
○
SOLUTION CONTENT. [cc./100g.]
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
pF.

FIGURE 60.

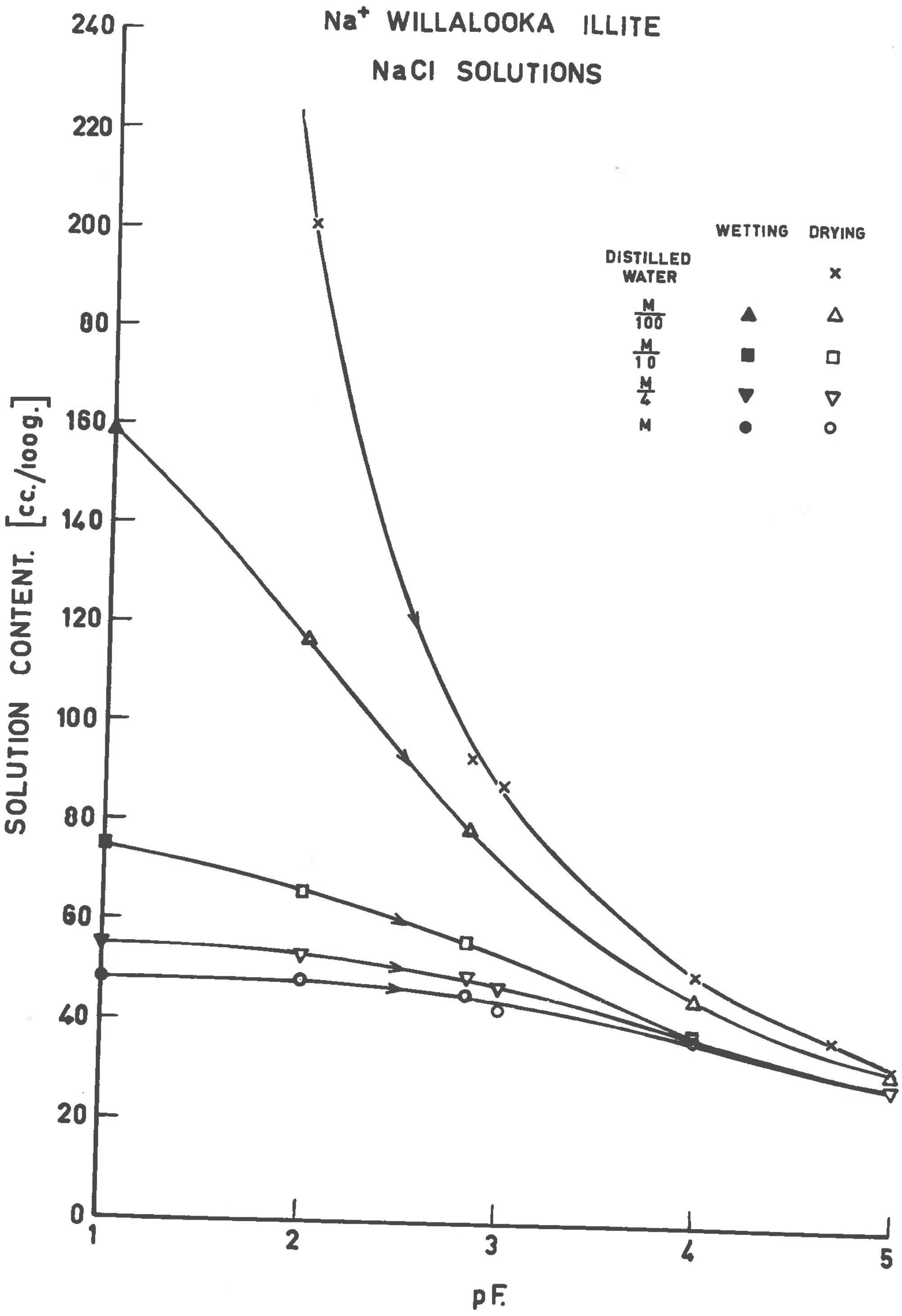

Na⁺ WILLALOOKA ILLITE
NaCl SOLUTIONS
WETTING
DRYING
DISTILLED WATER ×
M/100 ▲ △
M/10 ■ □
M/4 ▼ ▽
M ● ○
SOLUTION CONTENT. [cc./100g.]
0
20
40
60
80
100
120
140
160
80
200
220
240
1
2
3
4
5
pF.

FIGURE 61.

in solution content with increasing electrolyte concentration at pF 1 the sodium Willalooka gel shows an even more marked increase with increasing electrolyte concentration.

### Potassium Chloride Solutions.

The values of solution content obtained on wetting potassium Grundite and Willalooka illite cores to 100 cm suction of $\frac{N}{10}$ and $\frac{N}{100}$ potassium chloride solutions in comparison with those obtained on distilled water are shown in Table 14.

TABLE 14

EFFECT OF POTASSIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON WETTING TO pF 2

| | Solution Content pF 2 (cc/100g) | | |
|---|---|---|---|
| Concentration | Distilled water | $\frac{N}{100}$ | $\frac{N}{10}$ |
| Clay | | | |
| $K^+$ Grundite Illite | 54.7 | 52.4 | 48.1 |
| $K^+$ Willalooka Illite | 75.3 | 60.5 | 52.7 |

As for the sodium clays the swelling of the potassium Willalooka illite is far more sensitive to increasing electrolyte concentration than is the case for the potassium Grundite illite.

### Calcium Chloride Solution.

The effect of increasing concentrations of calcium chloride solution on the drying curve after wetting to pF 1 for calcium Grundite and Willalooka illites are shown in Figures 62 and 63 respectively. It is immediately obvious that variations in calcium chloride solution concentration between that of distilled water and molar have little if any effect on the solution uptake of the calcium illites and only for the 4 molar concentration is there any appreciable restriction. It is interesting to note, however, that this restriction in 4 molar is appreciably larger for the Grundite illite than the Willalooka illite presumably because the swelling of the Willalooka illite is already more severely restricted.

The effect of concentration of calcium chloride solution on the solution content on drying suspensions of the clay to pF 1 is shown in Table 15. These suspensions were made as for the sodium clay by shaking the powdered clay with distilled water and adjusting the concentration with 4 molar calcium chloride solution. The sodium → calcium Willalooka clay was obtained by calcium saturating a suspension of the sodium clay with molar calcium chloride, removing excess salt by washing with distilled water and then adjusting to the required concentrations.

TABLE 15

EFFECT OF CALCIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON DRYING SUSPENSIONS TO pF 1

| | Solution Content pF 1 (cc/100g) | | | |
|---|---|---|---|---|
| Concentration | Distilled water | $\frac{M}{100}$ | $\frac{M}{10}$ | M |
| Clay | | | | |
| $Ca^{++}$ Grundite Illite | 123 | 117 | 118 | 117 |
| $Ca^{++}$ Willalooka Illite | 188 | 165 | 173 | 179 |
| $Na^{+} \rightarrow Ca^{++}$ Willalooka Illite | 264 | 329 | 313 | 267 |

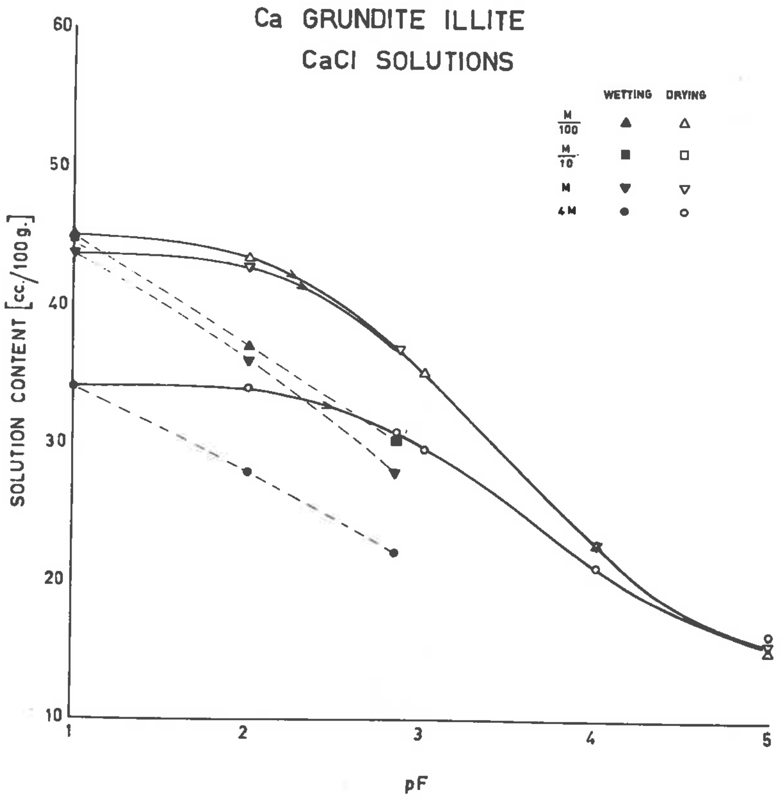


FIGURE 62.

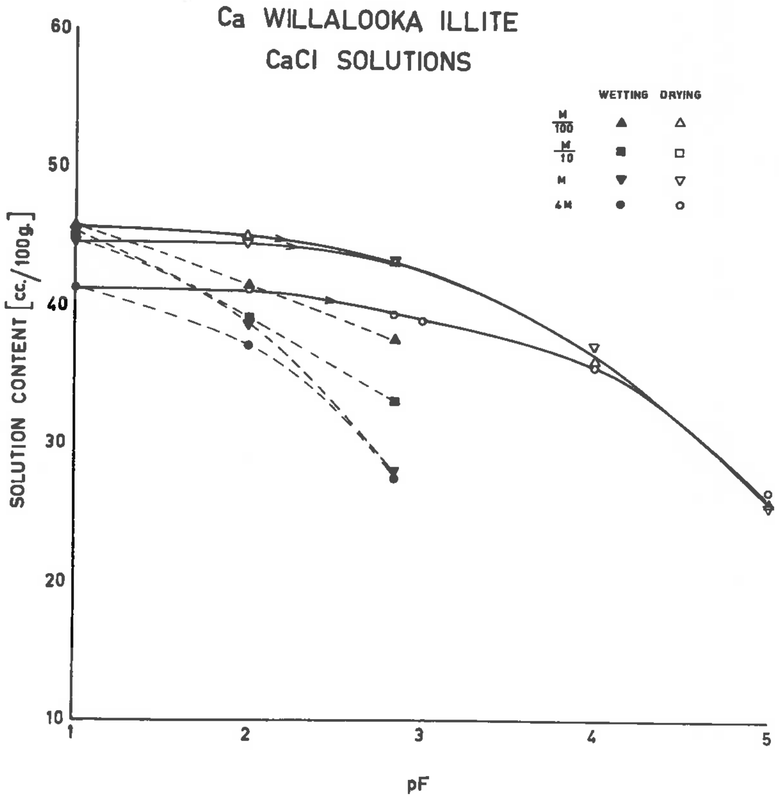


FIGURE 63.

Once again it is apparent that increase in concentration of calcium chloride solution has little effect in reducing the solution content of the calcium clays even at the higher values obtained by drying from suspension.

### 2.1.3. Discussion.

It is obvious that there is a marked difference in behaviour between the two illites studied. In dilute solutions the monovalent clays behave much as would be expected from diffuse double layer considerations with solution contents bearing some relationship to specific surface area and showing a marked dependence on both hydrostatic and osmotic components of the free energy. However, for concentrations of sodium chloride, greater than $\frac{N}{10}$ and when saturated with divalent cations it is apparent that the Willalooka illite is subject to a considerably greater restriction in swelling than is the Grundite illite. This is illustrated by the fact that for these situations the swelling of the Willalooka illite is reduced below that of the Grundite illite in spite of its specific surface area being approximately three times greater. This behaviour clearly indicates the existence of a potential barrier for the Willalooka illite. This barrier is exceeded in dilute solutions for the monovalent clays but not in higher concentrations or when saturated with divalent ions in much the same fashion as the intra crystalline swelling of the montmorillonite clays is restricted by a potential barrier in similar circumstances. It has been suggested in Section 2 of this thesis that Willalooka illite possesses a highly organized structure with the crystal sheets oriented on a microscale into domains and that almost the entire even dry porosity arises from average separations of the order of 28 Å between these oriented crystals. If this is so, the domain system has much in common with that of the montmorillonite crystal and provides an ideal situation for the operation of large electrostatic attractions as suggested by MacEwan (1948) with the exchangeable cations lying between the negatively charged clay plates. In these circumstances the volume of solution not directly associated with crystal surfaces would be less significant and a fairly close estimate of the film thickness developed on the clay surfaces should be obtained by dividing the water content by the specific surface area.

On wetting to pF 1 the water content of the calcium Willalooka cores is 45.0 cc/100g. Dividing by the specific surface area of the clay, 150 $m^2/g$, indicates an average film thickness of approximately 30 Å. Application of the swelling pore theory on the other hand leads to a value of 11 Å for the film thickness which is obviously incorrect if the surfaces are accepted as starting at an average of 28 Å apart, since the void volume of the clay-water system has more than doubled.

Holmes (1955) obtained a water content of 29 cc/100g for natural (divalent) Urrbrae B clay cores on the second wetting to pF 2. Since it appears from Section 2 that this clay has a similar high degree of orientation to that of the Willalooka illite, a good estimate of the average film thickness may also be obtained by dividing the water content by the specific surface area, 94 $m^2/g$. This leads to a value of 31 Å which is in excellent agreement with that calculated for Willalooka illite since although not shown in Holmes' data the Urrbrae B cores show negligible further water uptake between pF 2 and 0.

Sodium Willalooka illite takes up 48.2 cc/100g of normal sodium chloride solution at pF 1 which once again indicates a film thickness of the order of 30 Å, strongly suggesting the existence of a potential barrier at this point.

Although the intra-domain film thickness may be quite regular, it would not be measurable by X-ray diffraction techniques because of the randomness of the thickness of the illite crystals forming the domains.

The existence of this potential barrier is either lacking or less apparent for the Grundite illite since with its much smaller specific surface area it takes up as much water when calcium saturated as does Willalooka illite, more than the Urrbrae B cores, and shows a greater dependence of water content on hydrostatic suction. By the same token this clay appeared to have far less domain development than Willalooka illite and Urrbrae B clay with a continuous distribution of pores up to several hundred angstroms in diameter; from this it follows that an appreciable correction for swollen porosity may be necessary. Applying the swelling pore theory leads to a value of 34 Å for the calcium saturated clay on wetting to pF 1 which is again in good agreement with that calculated for the other clays.

The magnitude of these film thicknesses plus the lack of sensitivity of solution content to electrolyte concentrations below molar indicates quite clearly that diffuse double layer theories are not applicable to the swelling of the divalent illites.

The large water contents attained in dilute solutions by the sodium Willalooka cores, do, however suggest the possibility of the formation of diffuse double layers once the potential barrier has been exceeded. By reference to Figure 64 in which the values of film thickness calculated by dividing solution content by specific surface area are compared with the theoretical diffuse double layer values it can be seen that the agreement for low pF values is quite good. At higher pF values reorganization of structure probably causes the larger deviations. The disappearance of hysteresis from the water content-suction relationship for the sodium Willalooka clay in distilled water at low pF values indicates very little dependence on gel structure at these points.

For the sodium Grundite illite cores, however, the agreement with diffuse double layer theory by either method of calculation is not at all satisfactory (Figure 65) and the development of diffuse double layers appears to be far outweighed by structural configuration of the clay mass. It is reiterated that the pF 1 points are wetting points and the remainder drying. As hysteresis is still very evident for this clay at low pF values the effect of the structure developed on wetting may be to hinder the diffuse double layer development. Subsequently on drying the effect of this developed structure may be the reverse, increasing the amount of solution retained above that held on the clay surfaces and thereby masking to some extent the decrease in film thickness with increasing osmotic and hydrostatic suction.

It is apparent that on drying from the suspension state the formation of gel structures by mechanical interaction of the clay plates enables a considerable amount of additional solution to be enmeshed. The dependence of the solution contents obtained in this fasion on the method of preparation emphasises the futility of such procedures as a means of estimating film thicknesses for comparison with theoretical data. For

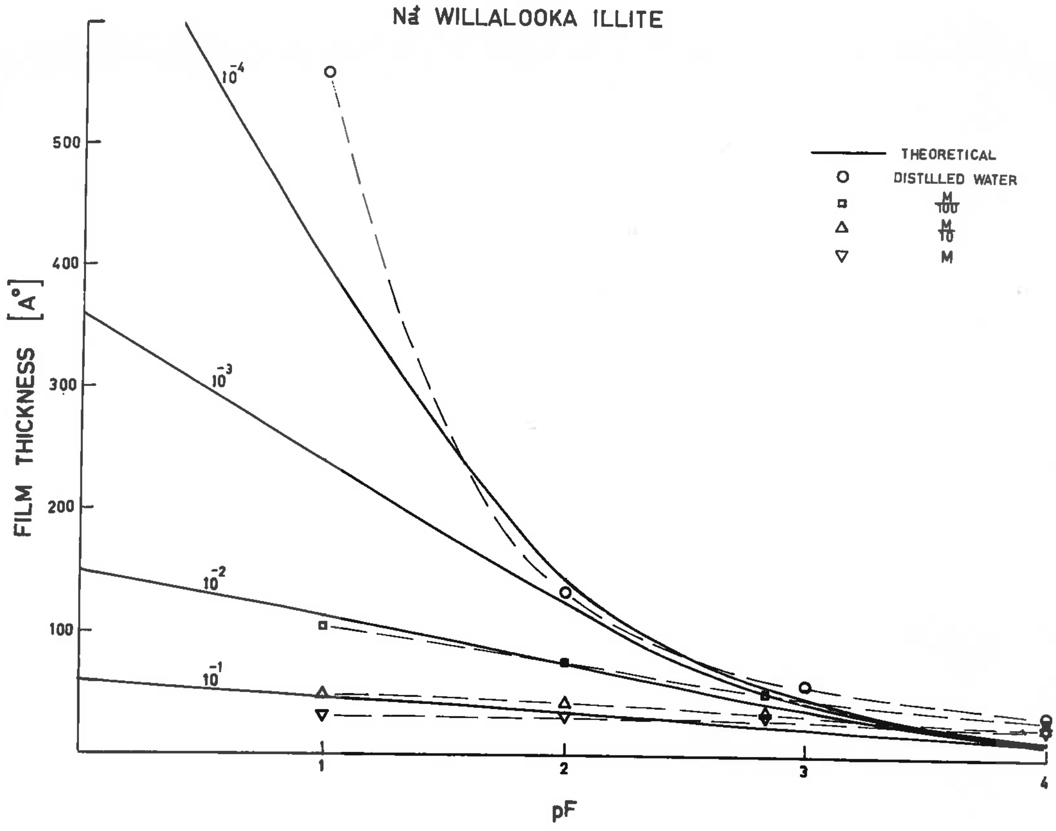


FIGURE 64.

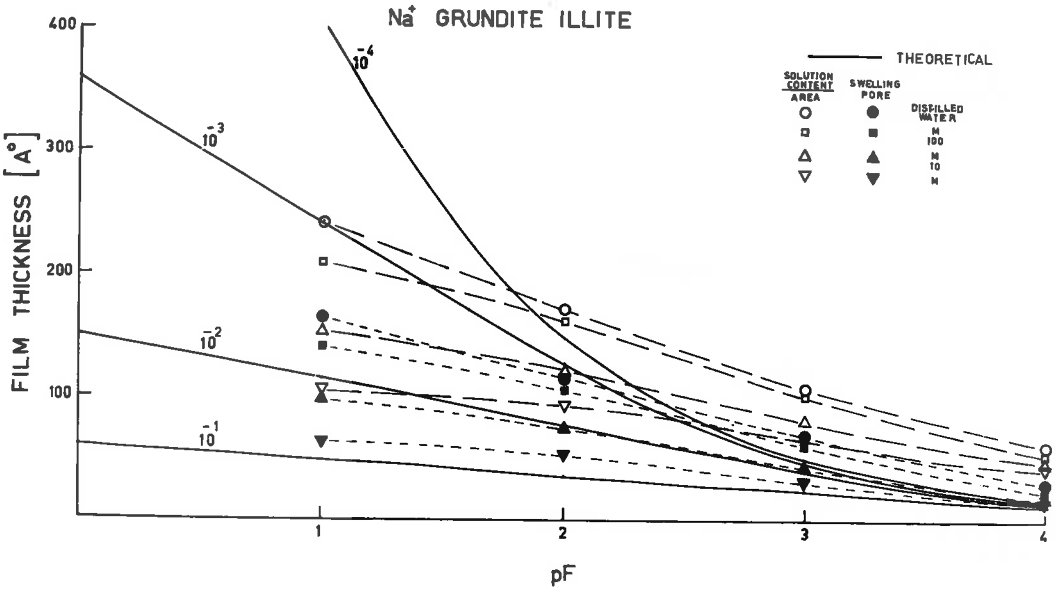


FIGURE 65.

the calcium clays this formation of gel structures appears to be unaffected by the concentration of electrolyte present which may be taken as an indication that the film thicknesses developed on the clay surfaces even in dilute solutions are not sufficient to effect the mechanical interaction of the clay particles. Contrasting with this lack of sensitivity to electrolyte concentration is the rapid decrease in solution content with increasing hydrostatic suction which undoubtedly arises from the collapse of the gel structure under mechanical force.

The larger solution contents obtained with the sodium → calcium Willalooka clay probably arises from a more open network of clay crystals, possibly resulting from the disruption of some domains. These domains are apparently reformed on drying since the sodium → calcium cores show the same behaviour as the original calcium cores.

The anomalous behaviour of the sodium Willalooka suspensions on drying to pF 1 at various concentrations is difficult to interpret. However, unpublished negative adsorption data of Quirk indicate the possible existence of positive edge charges for Willalooka illite. Consequently the addition of electrolyte to the dispersed sodium suspensions may by reducing diffuse double layer repulsion, enhance the formation of a stronger gel network by edge to face attractions.

The difference in the extent of the domain formation and consequent differences in behaviour on wetting between Willalooka illite, Urrbrae B clay and the Grundite illite must arise from a basic difference in morphology. One immediate possible explanation arises from the larger surface density of charge of the Grundite illite as shown in Table 16.

TABLE 16

SURFACE DENSITY OF CHARGE OF ILLITE CLAYS

| Clay | Grundite Illite | Urrbrae B Clay | Willalooka Illite |
|---|---|---|---|
| Surface Density of Charge ($\times 10^{-7}$ me/cm$^2$) | 4.4 | 3.0 | 2.7 |

The larger particle size of the Grundite illite could also influence the extent to which domain formation occurs on drying and in these circumstances the larger surface density of charge and consequent greater hydration energy available may be capable of expanding the domains past the potential barrier even in the divalent case. This, of course, is in reverse to the conclusions of Greene-Kelly (1953) regarding the dependence of inter lamellar swelling of the layer lattice silicates on surface density of charge but it is pointed out that the initial distance of separation of crystals forming a domain (28 Å) appears to be much greater than those discussed by Greene-Kelly.

Alternatively the larger average film thickness for Grundite illite in the divalent ion and stronger sodium chloride solution cases could arise from the development of thicker layers on the external surfaces of the domains where there is no potential barrier since no opposing parallel crystal. This external domain surface area would appear to be larger for Grundite illite than for Willalooka illite.

If the suggestion of Barrer and McLeod (1954) regarding the movement of clay particles by surface tension forces on the adsorption of liquid nitrogen is correct, then it is apparent that the interparticle bonding for Grundite illite is much weaker than for the other two illitic clays since these show no characteristic shoulder in the nitrogen desorption isotherm.

## 2.3 Montmorillonites.

### 2.3.1. Distilled Water.

The water content-suction relationships obtained for Wyoming Bentonite and Redhill montmorillonites when saturated with various cations are shown in Figures 66 to 69 and 70 to 73 respectively.

The low angle X-ray diffraction studies of Norrish and Quirk (1954) and Norrish (1954) have shown that whilst the internal spacing of divalent montmorillonites is restricted by a potential barrier to a maximum d(001) = 19 Å, sodium and other monovalent ion montmorillonites are capable of expanding internally past this barrier to separations of at least several hundred angstroms. This property is clearly shown in the difference between the monovalent and divalent clays in the present work. Both sodium montmorillonites show a tremendous water uptake at low pF values accompanied by the formation of gel or thixotropic like structures. An interesting difference between the two montmorillonites is that the sodium Wyoming Bentonite cores retain their rigidity to very high water contents whilst the Redhill cores become fluid and collapse at water contents approaching 1000 cc/100g. This indicates a stronger thixotropic tendency for the Wyoming Bentonite possibly as a result of its larger particle size.

Since the divalent montmorillonites show limited intracrystalline expansion (maximum d(001) = 19 Å) the magnitude of the external surface area of the crystals would be expected to play an important part in determining the water content at low pF values ($pF < 5$). At

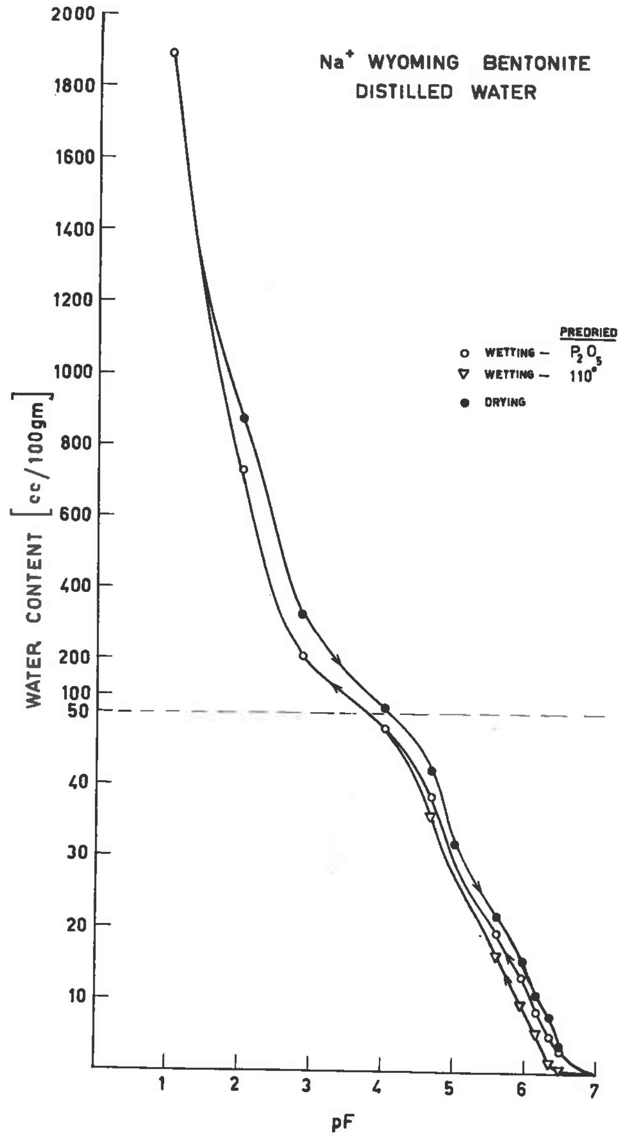


FIGURE 66.

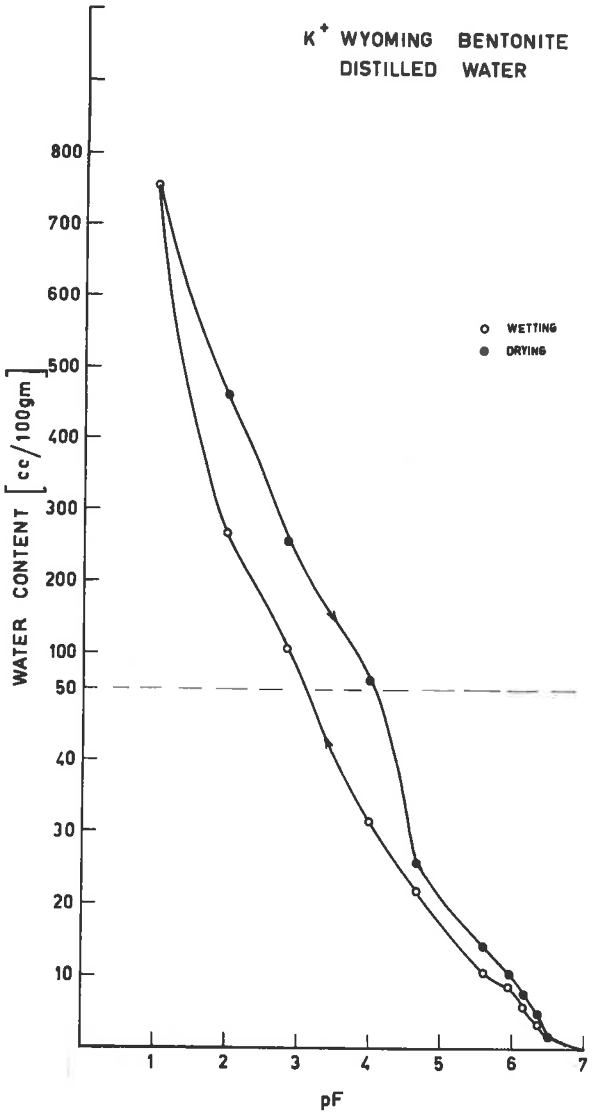


FIGURE 67.

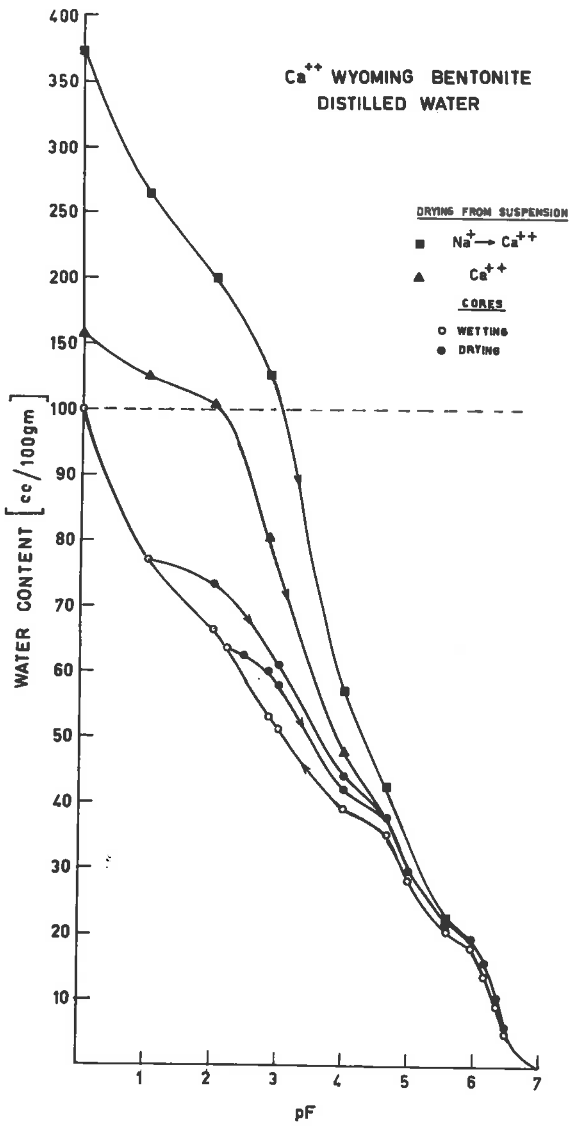


FIGURE 68.

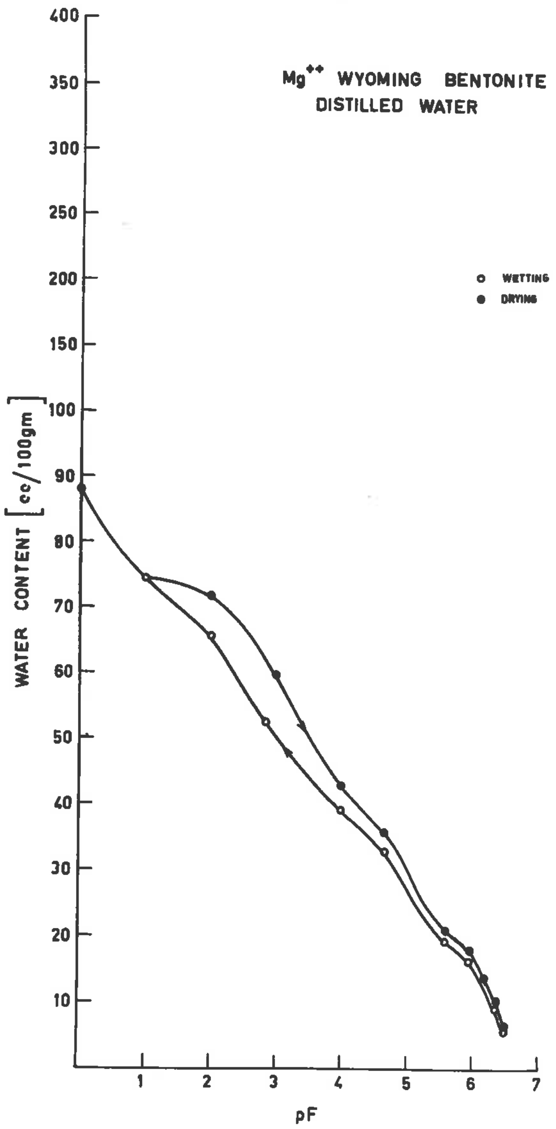


FIGURE 69.

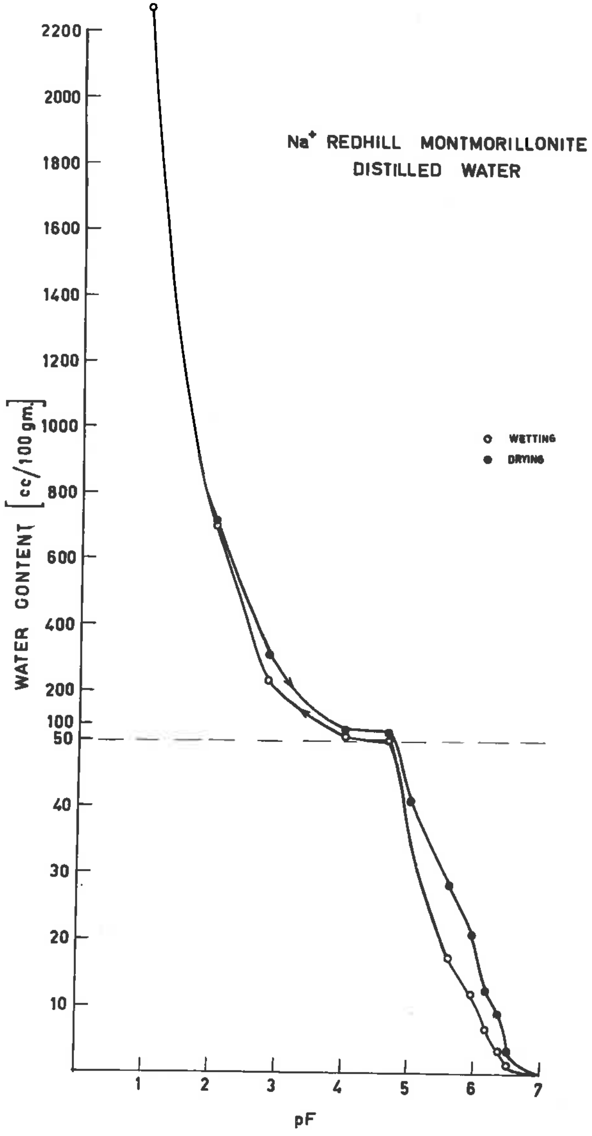


FIGURE 70.

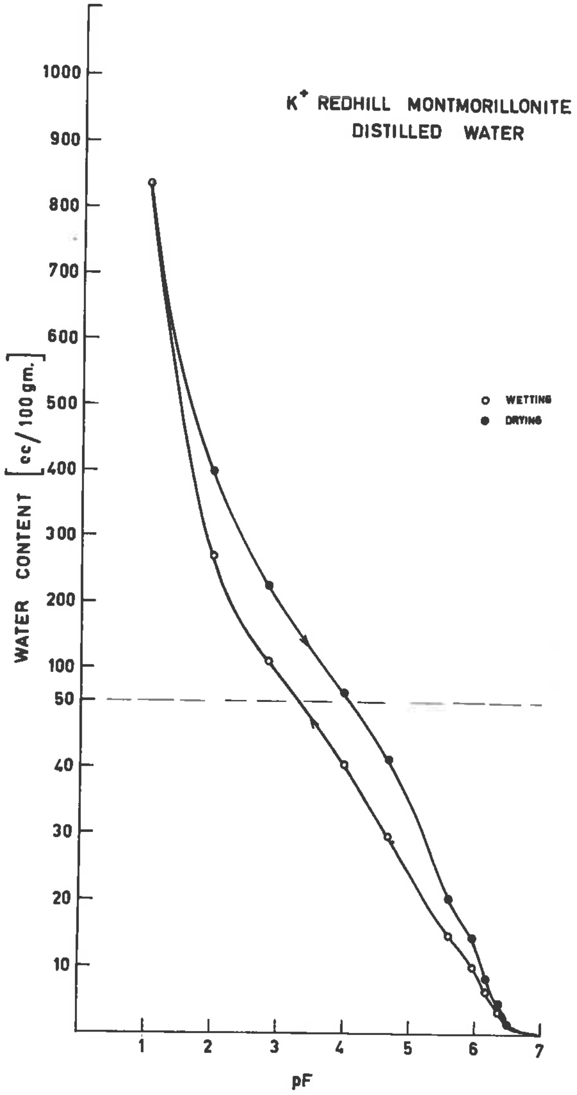


FIGURE 71.

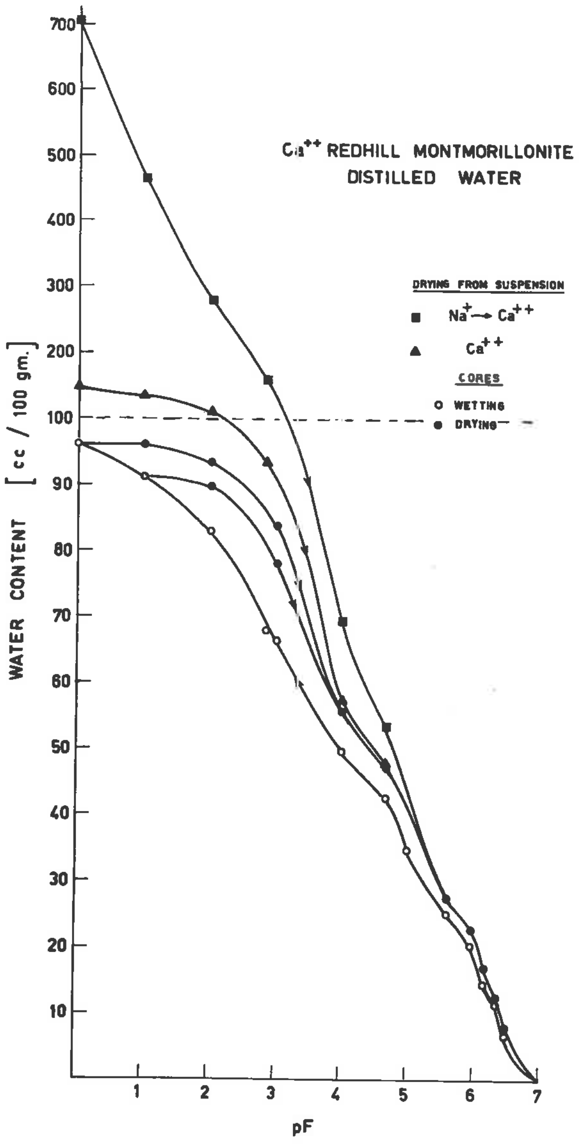


FIGURE 72.

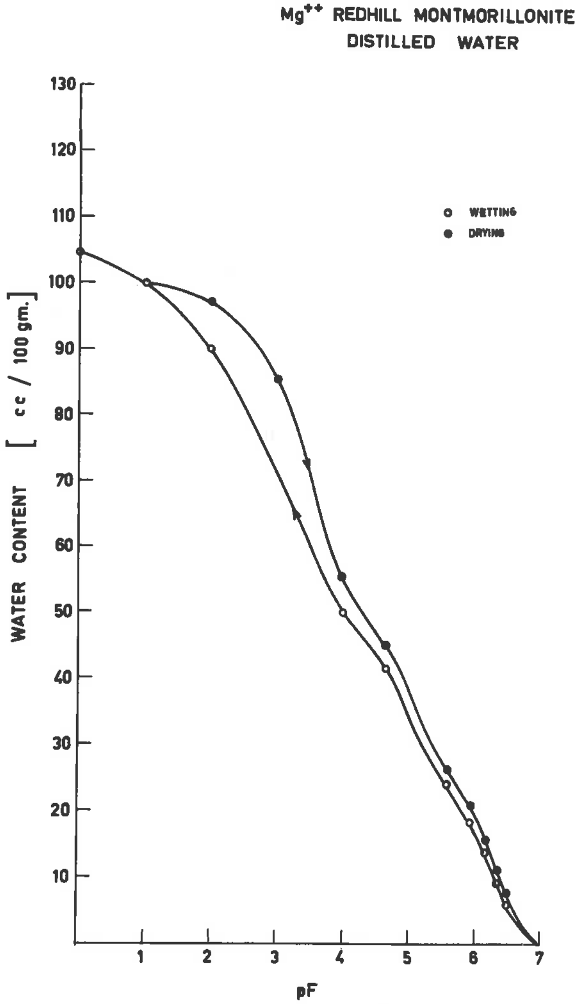


FIGURE 73.

first sight this appears to be the case with Redhill montmorillonite retaining appreciably more water. However, the differences at high water contents after allowing for the intercalated water (34 cc/100g and 29 cc/100g for calcium Wyoming Bentonite and Redhill montmorillonite respectively) appear to be less than might be expected since the external surface area of the Redhill montmorillonite is more than double that of Wyoming Bentonite. In addition the water uptake of the divalent Wyoming Bentonite cores shows a marked dependance on applied suction between pF 1 and 0 whilst that of the Redhill montmorillonite is less susceptible. These considerations are discussed further after the presentation of the data for the additional montmorillonites.

It can be seen from Figure 66 that the adsorption of water vapour at high pF values by the sodium Wyoming Bentonite is markedly dependant on the previous drying procedure whether by evacuation over phosphorus pentoxide or by oven drying at 110°C. Despite only small differences in actual weight loss between the two drying procedures the difference on readsorption is maintained to pF values less than 5 but disappears after the completion of the initial crystalline swelling to d(001) = 19 Å. Presumably the heating process results in the collapse of more interlamellar spacings. This dependance of the adsorption isotherm for sodium Wyoming Bentonite on the predrying procedure is similiar to that observed by Mooney, Keenan and Wood (1952). This effect was not noticed for the divalent clays in the present work and this possibly results from the greater hydration energy of the divalent ions either preventing the collapse of internal spacings till much higher temperatures or being more capable of expanding them after collapse.

The formation of discrete integral layers of water molecules within the interlamellar spacing gives rise to change in slope of the sorption isotherms in the high pF range (Bradley, Grim and Clark, 1937; Mering, 1946; Mooney, Keenan and Wood, 1952; and Norrish, 1954). For the divalent calcium and magnesium ions the octahedral co-ordination of hydration water about the ions prevents the formation of an integral single layer (Mering, 1946) below 0.32 relative vapour pressure (pF 6.2). The completion of the second and third interlamellar water layers are discernable from the change in slope of the sodium calcium and magnesium isotherms at 0.51 and 0.96 relative vapour pressure (pF 6.0 and 4.7) respectively.

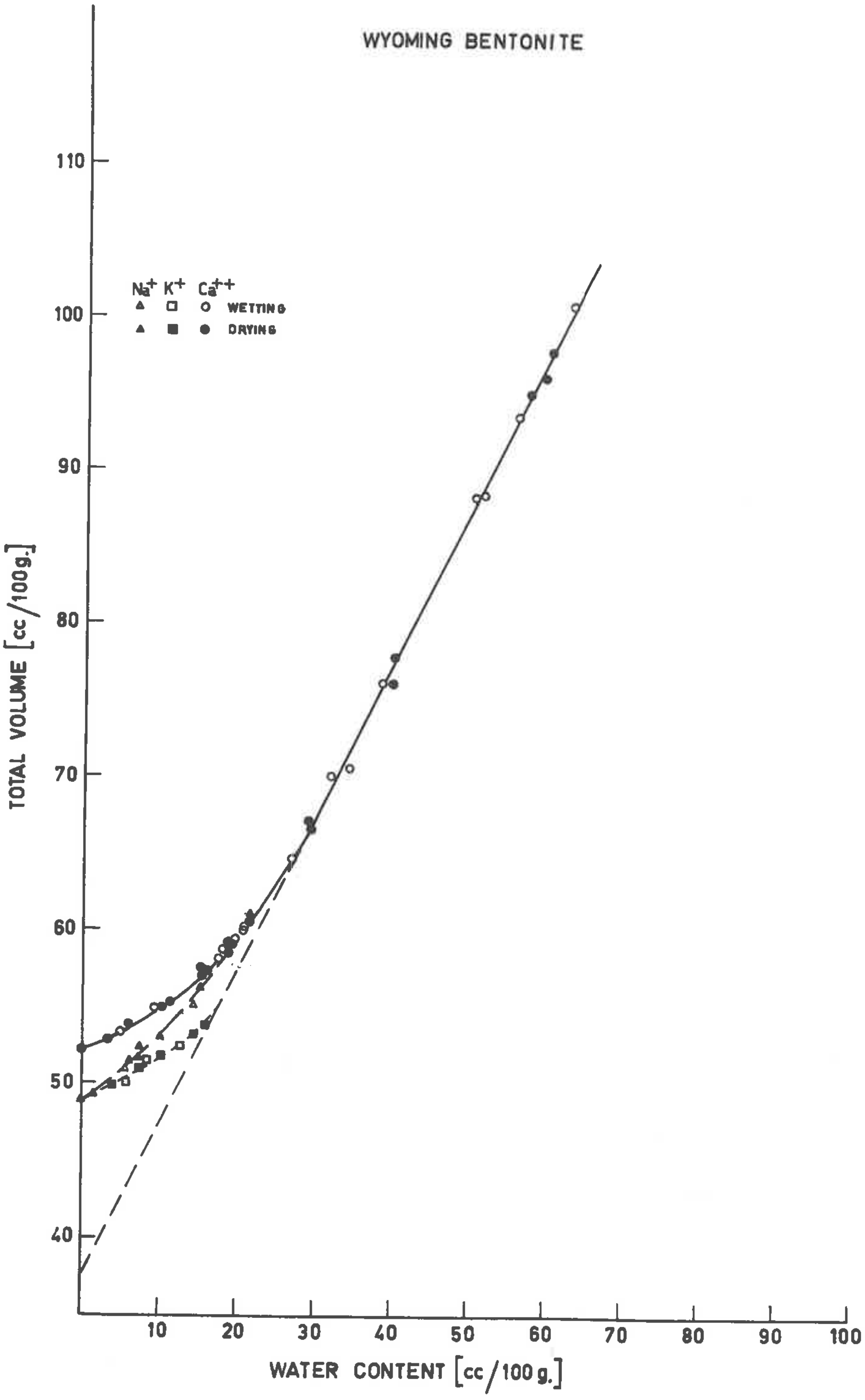
By pF 4.5 this internal hydration of the clay lattice is completed and thereafter macroswelling occurs in the sodium clays as the potential barrier is exceeded whilst the remaining uptake of the divalent clays is determined by external surface area and porosity considerations.

The crystalline swelling of the potassium montmorillonites only proceeds to d(001) = 15 Å (Norrish, 1954); corresponding to the flattening of the isotherm between 0.51 and 0.76 relative vapour pressure (pF 6.0 and 5.6) but thereafter the cores do exhibit macroswelling in contrast with the findings of Norrish.

The present results for adsorption at high pF values therefore appear to be in agreement with the stepwise hydration of the crystal lattice as observed by previous workers using X-ray diffraction techniques.

In addition to the relationships obtained using the clay cores the effect of drying from the gel state was investigated for both calcium clays. One gel sample was obtained by shaking the calcium saturated montmorillonite powders with distilled water as previously described and the other by calcium saturating a suspension of the sodium saturated clays using molar calcium chloride and then washing with distilled water to remove excess salt. The resultant gels had initial water contents of 373 cc/100g and 167 cc/100g for the Wyoming Bentonite and 709 cc/100g and 150 cc/100g for the Redhill montmorillonite for the sodium → calcium and calcium samples respectively. From Figures 68 and 72 it can be seen that the effect of previous history is not removed until pF values in excess of 4.5, once again illustrating the complexity of the problem of determining film thicknesses for clays by drying from the gel state.

The experimentally determined relationship between total volume and water content for Wyoming Bentonite and Redhill montmorillonite when saturated with various cations are shown in Figures 74 and 75 respectively. The decrease in volume does not cease with divergence from the normal shrinkage line as for the kaolinite and illite cores but continues with decreasing water content to the value obtained for the oven dry volume of the cores. For sodium, calcium and magnesium Wyoming Bentonite the divergence from the normal shrinkage line occurs at a water content of approximately 24 cc/100g and for potassium Wyoming Bentonite at approximately 16 cc/100g both values indicating that air entry on drying first occurs at a pF value of approximately 5.4. The final apparent dry volume for the monovalent clays (49 cc/100g) is appreciably less than that for the divalent clays (52 cc/100g) which



WYOMING BENTONITE
Na+ K+ Ca++
WETTING
DRYING
TOTAL VOLUME [cc/100g.]
110
100
90
80
70
60
50
40
10
20
30
40
50
60
70
80
90
100
WATER CONTENT [cc/100g.]

FIGURE 74.

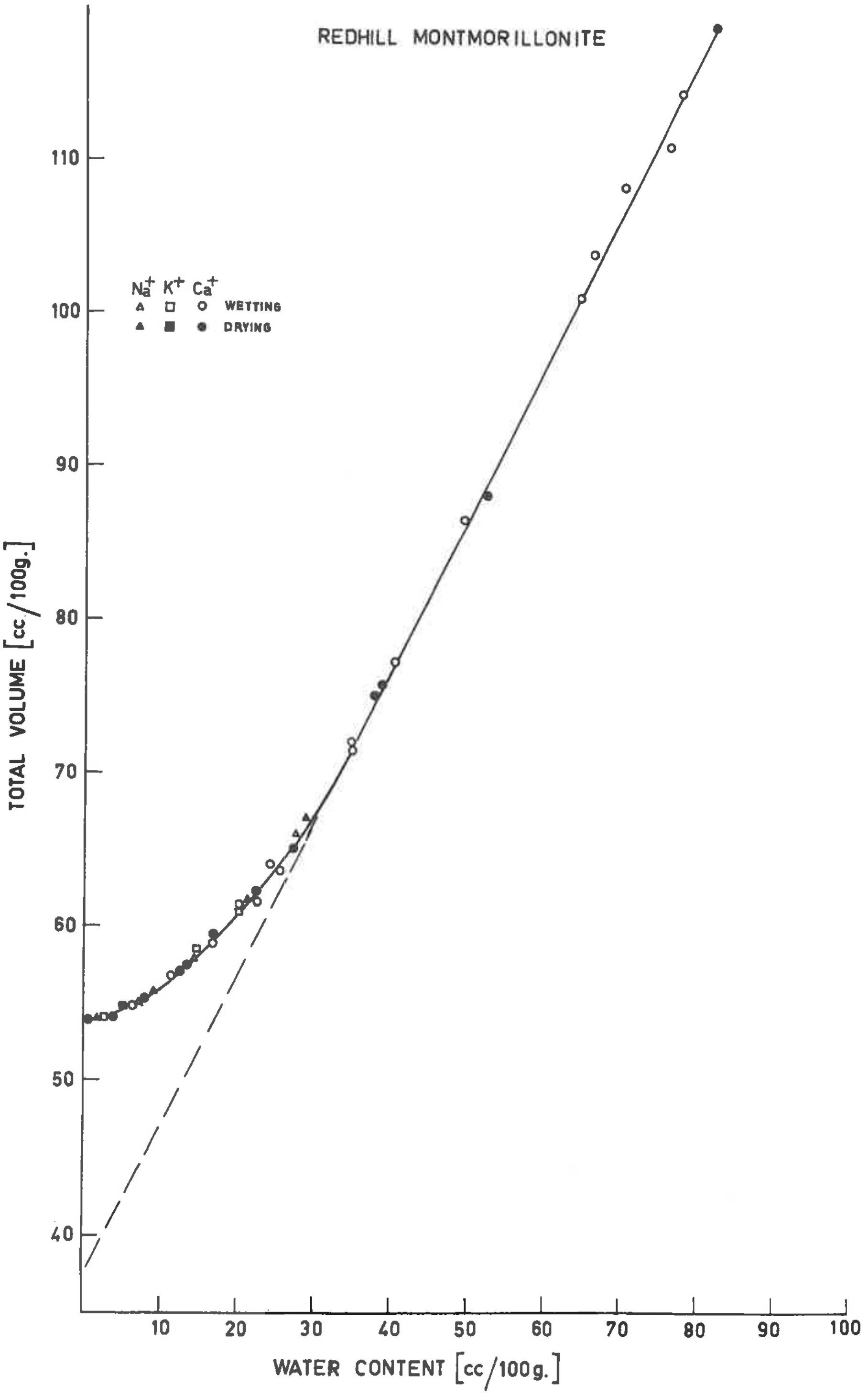

REDHILL MONTMORILLONITE
Na⁺ K⁺ Ca⁺
△ □ ○ WETTING
▲ ■ ● DRYING
TOTAL VOLUME [cc/100g.]
110
100
90
80
70
60
50
40
10
20
30
40
50
60
70
80
90
100
WATER CONTENT [cc/100g.]

FIGURE 75.

seems to confirm the suggestion that more interlamellar spacings are proped apart by residual water molecules in the divalent than in the monovalent case. The large surface areas obtained by Brooks (1955) for calcium Wyoming Bentonite on particl desorption also supports this idea.

For the Redhill montmorillonite the total volume - water content curve was found to be the same within the limits of experimental error regardless of the exchangeable cation present. The divergence from the normal shrinkage line occurs at a water content of approximately 28 cc/100g corresponding on the drying curves to a pF value of approximately 5.6 for the sodium, calcium and magnesium clays and to pF 5.3 for the potassium clay.

The values of pF for initial air entry into the calcium montmorillonite cores indicate maximum pore sizes of less than 50 Å equivalent cylindrical radius for these cores. Since from the nitrogen studies the dry cores appear to have a considerable volume of pores with equivalent cylindrical radii of several hundred angstroms it may be concluded that considerable internal accommodation of swelling producing an effective reduction in pore dimensions has occured. This consideration is later discussed in more detail.

It is interesting to note that the value of clay particle volume calculated from specific gravity determinations (38.6 cc/100g and 38.8 cc/100g for Wyoming Bentonite and Redhill montmorillonite respectively) are slightly greater than the 37.5 cc/100g obtained in each case by extrapolation of the normal shrinkage line.

## 2.3.2. Effect of Electrolyte Concentration. Sodium Chloride Solutions.

The effect of concentration of sodium chloride solution on the drying curves after wetting to pF 1 for sodium Wyoming Bentonite and sodium Redhill montmorillonite are shown in Figures 76 and 77 respectively. The distilled water curves are included for comparison. In Table 17 the solution contents on wetting to pF 1 for these and the additional montmorillonites are listed.

TABLE 17

EFFECT OF SODIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON WETTING TO pF 1

| | Solution Content pF 1 (cc/100g) | | | | | |
|---|---|---|---|---|---|---|
| Concentration | Distilled water | $\frac{N}{100}$ | $\frac{N}{10}$ | $\frac{N}{4}$ | N | Nitrogen Surface Areas ($m^2/g$) |
| Clay | | | | | | |
| $Na^+$ Wyoming Bentonite | 1890 | 763 | 488 | 354 | 95.3 | 48.2 |
| $Na^+$ Redhill Montmorillonite | 2274 | 635 | 444 | 319 | 134 | 104 |
| $Na^+$ Maaza Montmorillonite | | 412 | 180 | 147 | 87.9 | 66.6* |
| $Na^+$ Panther Creek Montmorillonite | | 688 | 398 | 288 | 99.8 | 68.9* |
| $Na^+$ Tidinit Montmorillonite | | 689 | 369 | 188 | 89.5 | 93.2* |
| $Na^+$ Volclay Bentonite | | 904 | 605 | 475 | 94.2 | 32.5* |

* Surface Area of calcium clay

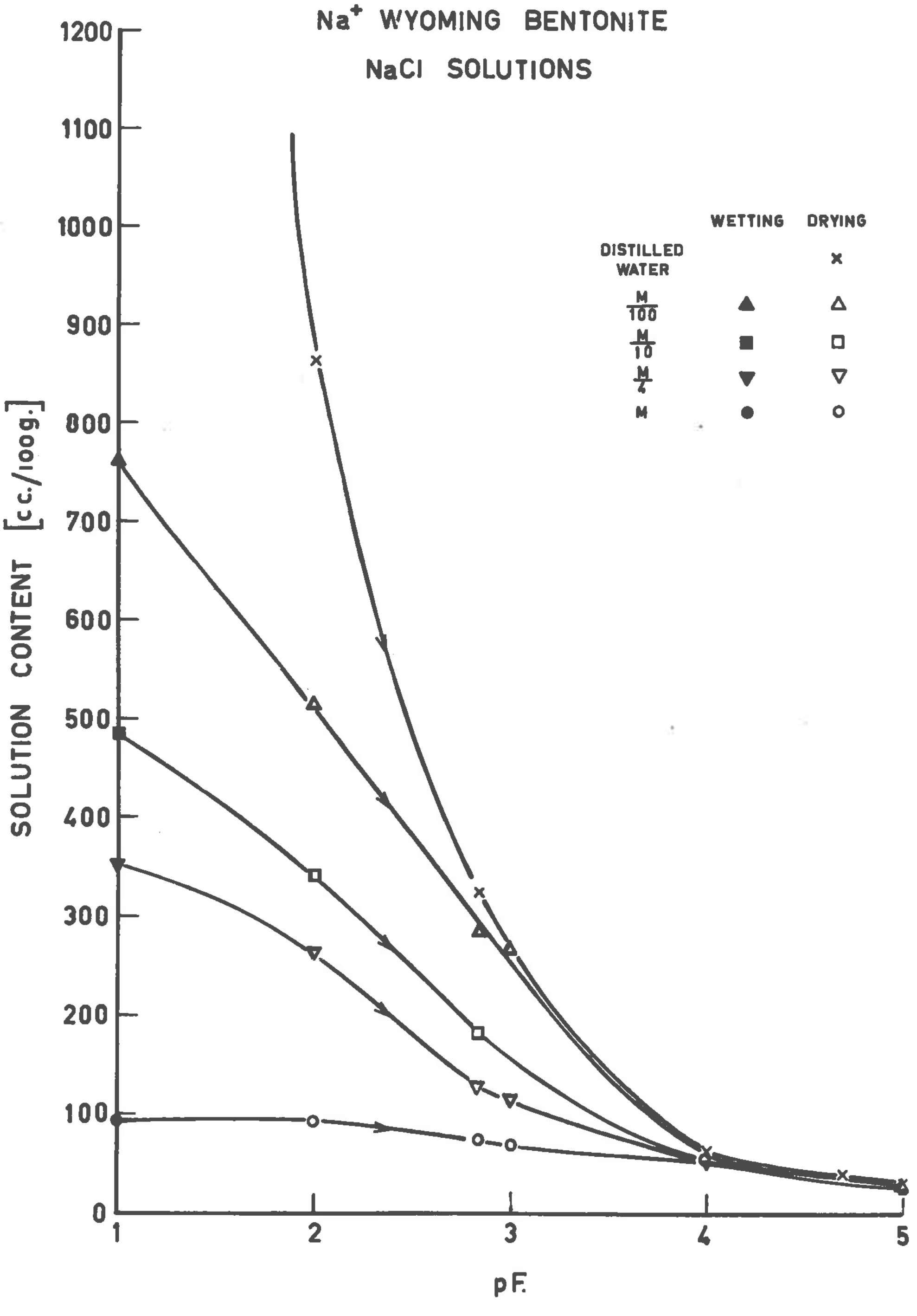

Na⁺ WYOMING BENTONITE
NaCl SOLUTIONS
WETTING
DRYING
DISTILLED WATER ×
M/100 ▲ △
M/10 ■ □
M/4 ▼ ▽
M ● ○
SOLUTION CONTENT [c.c./100g.]
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
1
2
3
4
5
pF.

FIGURE 76.

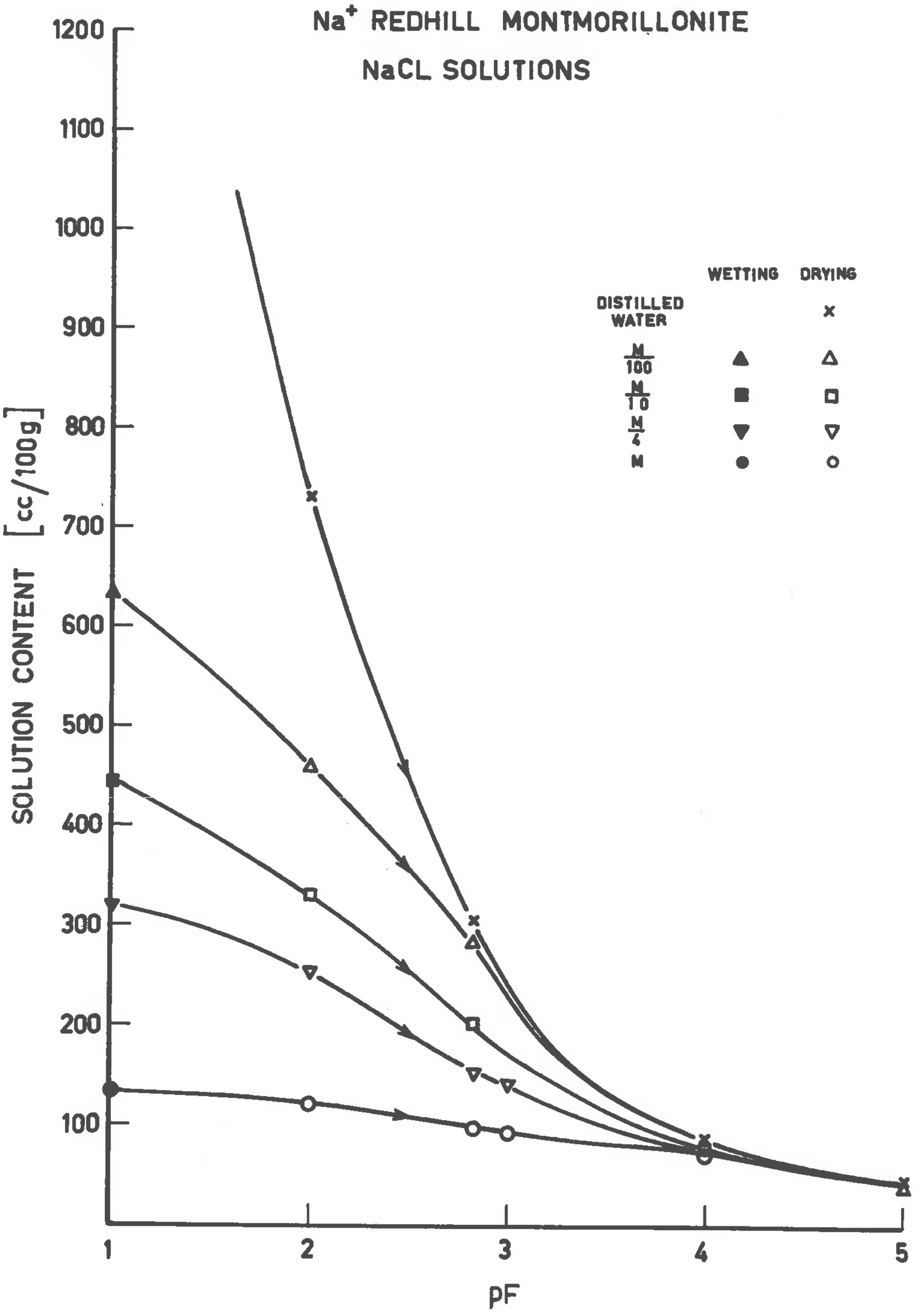

Na$^+$ REDHILL MONTMORILLONITE
NaCL SOLUTIONS
SOLUTION CONTENT [cc/100g]
1200
1100
1000
900
800
700
600
500
400
300
200
100
1
2
3
4
5
pF
WETTING
DRYING
DISTILLED WATER
×
M/100
▲
△
M/10
■
□
M/4
▼
▽
M
●
○

FIGURE 77.

The magnitudes of the solution contents decrease rapidly with increasing electrolyte concentration as would be expected both from diffuse double layer theory and the X-ray measurements of Norrish (1954). The values in molar sodium chloride are not, however, in proportion to the external surface area of the clays and there are wide variation in values between the clays for more dilute solutions, indicating that factors other than film thickness on the clay surface are influencing solution uptake.

From Figures 76 and 77 it can be seen that the osmotic component of the free energy lowering has relatively little effect for sodium Wyoming Bentonite and Redhill montmorillonite above pF 4.

An attempt to measure the actual internal spacing of the sodium Wyoming Bentonite on $\frac{N}{4}$ and $\frac{N}{100}$ sodium chloride solutions by filling glass capillaries with the swollen gels and using low angle X-ray diffraction techniques was made. In each case only diffuse patterns were obtained.

The approach to equilibrium for the sodium Wyoming Bentonite and Redhill Montmorillonite cores on wetting to pF 2 and subsequent wetting to pF 1 with various concentrations of sodium chloride solutions are shown in Figure 78.

The effect of concentration of sodium chloride on the solution content on drying suspensions to pF 1 is shown in Table 18. The suspensions were prepared by shaking samples of the sodium clays with distilled water and adjusting to the desired concentration by the addition of 2N sodium chloride solution.

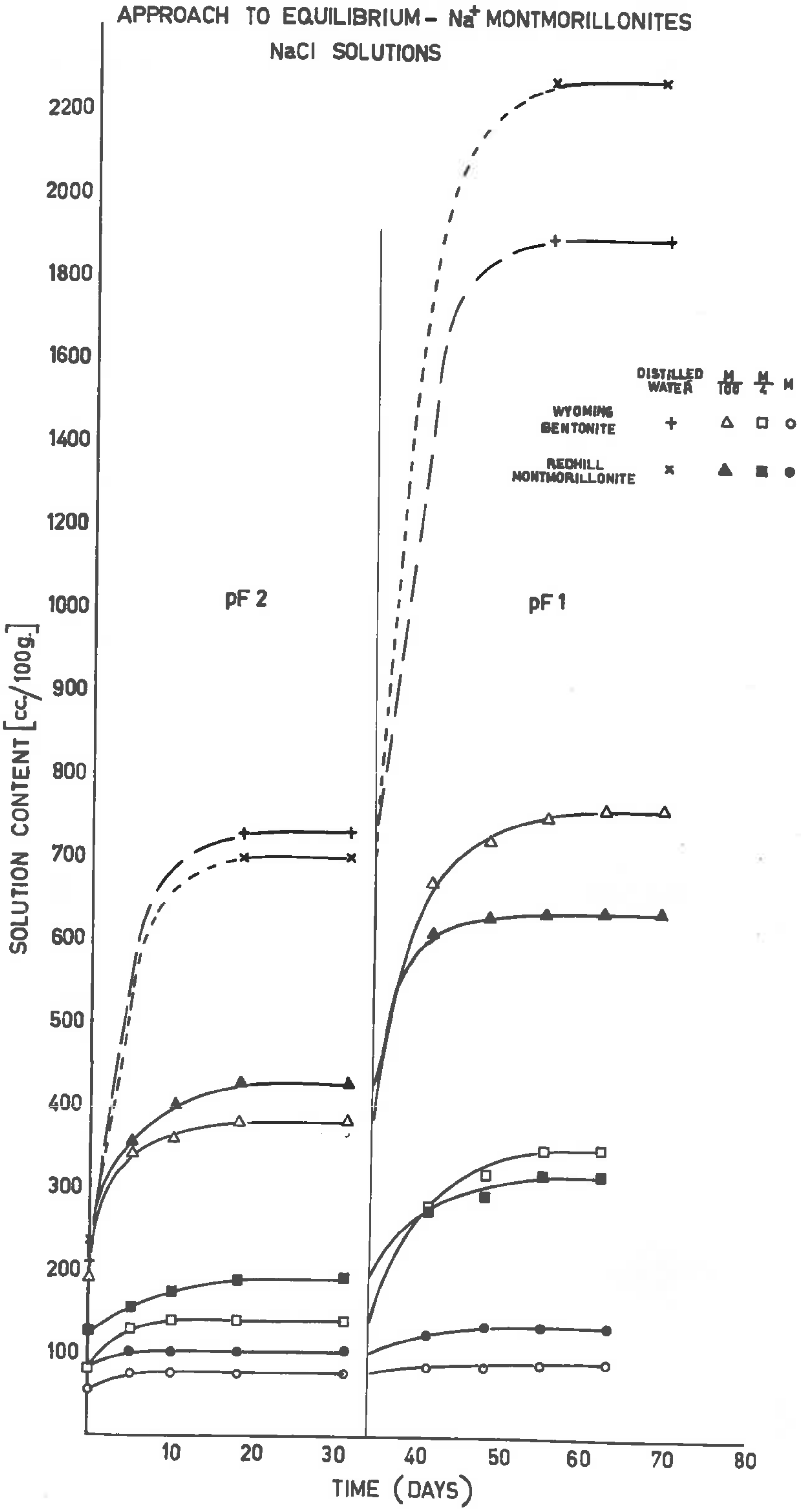

APPROACH TO EQUILIBRIUM - Na⁺ MONTMORILLONITES
NaCl SOLUTIONS
SOLUTION CONTENT [cc/100g.]
2200
2000
1800
1600
1400
1200
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
TIME (DAYS)
pF 2
pF 1
DISTILLED WATER
M/100
M/4
M
WYOMING BENTONITE
+ △ □ ○
REDHILL MONTMORILLONITE
× ▲ ■ ●

FIGURE 78.

## TABLE 18

## EFFECT OF SODIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON DRYING SUSPENSIONS TO pF 1

| | Solution Content pF 1 (cc/100g) | | | |
|---|---|---|---|---|
| Concentration | $\frac{N}{100}$ | $\frac{N}{10}$ | $\frac{N}{4}$ | N |
| Clay | | | | |
| $Na^+$ Wyoming Bentonite | 937 | 908 | 827 | 688 |
| $Na^+$ Redhill Montmorillonite | 784 | 1020 | 1060 | 892 |

The dominance of gel structure formation in determining solution retention is evident, particularly in view of the large solution contents retained in N sodium chloride solution compared with those taken up by the cores under the same conditions.

### Potassium Chloride Solution.

The values of solution content obtained on wetting potassium Wyoming Bentonite and Redhill montmorillonite cores to 100 cm suction on $\frac{N}{10}$ and $\frac{N}{100}$ potassium chloride solutions in comparison with those obtained on distilled water are shown in Table 19.

## TABLE 19

## EFFECT OF POTASSIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON WETTING TO pF 2

| | Solution Content pF 2 (cc/100g) | | |
|---|---|---|---|
| Concentration | Distilled water | $\frac{N}{100}$ | $\frac{N}{10}$ |
| Clay | | | |
| $K^+$ Wyoming Bentonite | 268 | 193 | 72.5 |
| $K^+$ Redhill Montmorillonite | 269 | 157 | 89.5 |

Although both clays appear to be well restricted by the potential barrier in $\frac{N}{10}$ potassium chloride solution at this suction, it is apparent that a certain amount of macroswelling has occurred in the $\frac{N}{100}$ solution.

### Calcium Chloride Solutions.

The effect of concentration of calcium chloride solution on the drying curve after wetting to pF 1 for calcium Wyoming Bentonite and Redhill montmorillonite are shown in Figures 79 and 80 respectively. The effect of concentration on the calcium chloride solution uptake at pF 1 for these two clays and also the additional montmorillonites are given in Table 20.

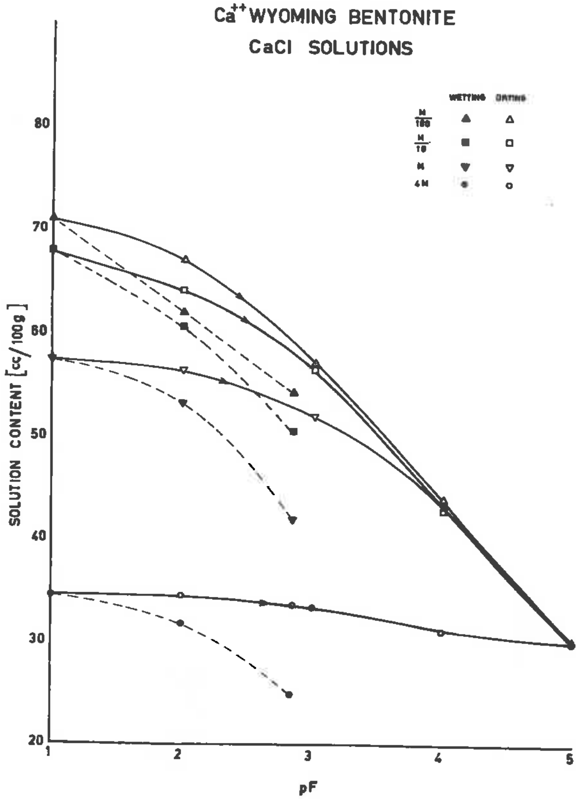


FIGURE 79.

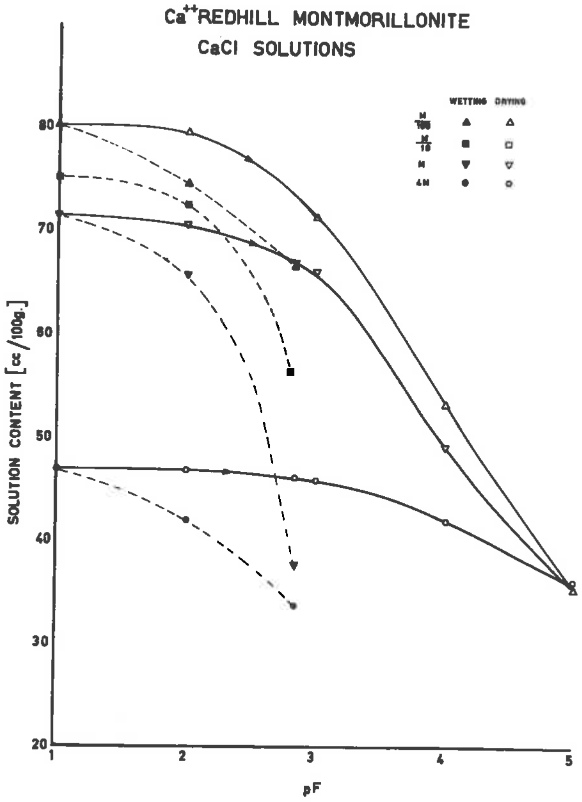


FIGURE 80.

## TABLE 20

## EFFECT OF CALCIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON WETTING TO pF 1

| | Solution Content pF 1 (cc/100g) | | | | |
|---|---|---|---|---|---|
| Concentration | Distilled water | $\frac{M}{100}$ | $\frac{M}{10}$ | M | 4 M |
| Clay | | | | | |
| $Ca^{++}$ Wyoming Bentonite | 77.0 | 70.9 | 67.9 | 57.4 | 34.4 |
| $Ca^{++}$ Redhill Montmorillonite | 91.2 | 80.2 | 75.0 | 71.5 | 46.9 |
| $Ca^{++}$ Maaza Montmorillonite | 59.9 | 58.1 | 57.4 | 53.4 | 40.0 |
| $Ca^{++}$ Panther Creek Montmorillonite | 68.1 | 63.5 | 59.8 | 56.7 | 36.1 |
| $Ca^{++}$ Tidinit Montmorillonite | 62.0 | 60.8 | 58.8 | 56.5 | 40.7 |
| $Ca^{++}$ Volclay Bentonite | 74.6 | 71.4 | 66.0 | 55.0 | 30.8 |

Although there are varying small decreases in solution uptake at pF 1 between those in distilled water and those in $\frac{M}{10}$ calcium chloride solution it is obvious that concentrations of the order of M and sometimes even 4M are necessary to cause appreciable restriction in swelling for these divalent montmorillonites. It is interesting to note that the hysteresis effect at pF 2.84 is significantly greater for the M than for the less concentrated solutions particularly in the case of the Redhill montmorillonite.

After weighing, the cores which had been wet to pF 1 with calcium chloride solutions, were soaked overnight in distilled water and their chloride contents determined by titration with silver nitrate solutions. The volume of solution in the cores from which the chloride ions were excluded (Schofield, 1947) was calculated and these values are shown in Table 21.

TABLE 21

CHLORIDE EXCLUSION BY MONTMORILLONITE IN CALCIUM CHLORIDE SOLUTIONS

| Concentration | Chloride Exclusion (cc/100g) | | | | Intracrystalline Volume (cc/100g) | |
|---|---|---|---|---|---|---|
| | 4M | M | $\frac{M}{10}$ | $\frac{M}{100}$ | | |
| d(001)* | 15.4 | 18.5 | 18.9 | 18.9 | 15.4 | 19.0 |
| Clay | | | | | | |
| Ca$^{++}$ Wyoming Bentonite | 8.3 | 18.1 | 27.0 | 36.9 | 18.1 | 32.5 |
| Ca$^{++}$ Redhill Montmorillonite | 9.4 | 18.8 | 28.0 | 59.2 | 16.5 | 29.8 |
| Ca$^{++}$ Maaza Montmorillonite | 6.5 | 13.5 | 22.5 | 27.0 | 17.1 | 30.7 |
| Ca$^{++}$ Panther Creek Montmorillonite | 7.4 | 17.4 | 25.7 | 38.3 | 17.3 | 31.1 |
| Ca$^{++}$ Tidinit Montmorillonite | 8.0 | 16.3 | 23.7 | 33.2 | 16.7 | 30.0 |
| Ca$^{++}$ Volclay Bentonite | 8.1 | 19.6 | 25.8 | 36.4 | 18.2 | 32.7 |

* Norrish (1954)

It is interesting to note that the chloride ions are capable of entering the intracrystalline spacings certainly at concentrations as low as $\frac{M}{10}$ indicating that very little development of diffuse double layers has occurred.

The effect of electrolyte concentration on the solution content on drying suspensions of calcium Wyoming Bentonite and Redhill montmorillonite to pF 1 is shown in Table 22.

TABLE 22

EFFECT OF CALCIUM CHLORIDE CONCENTRATION ON SOLUTION CONTENT ON DRYING SUSPENSIONS TO pF 1

| | Solution Content pF 1 (cc/100g) | | |
|---|---|---|---|
| Concentration | $\frac{M}{100}$ | $\frac{M}{10}$ | M |
| Clay | | | |
| $Ca^{++}$ Wyoming Bentonite | 142 | 141 | 130 |
| $Ca^{++}$ Redhill Montmorillonite | 166 | 161 | 157 |

These suspensions were made by shaking samples of the powdered calcium saturated clays with distilled water and adding sufficient 4 M calcium chloride solution to adjust the concentrations to the desired levels. Once again the solution content appears to be determined more by the gel structure formed than by the concentration of electrolyte present.

2.3.3. Discussion.

In terms of the calculation of film thickness developed on the clay surfaces the montmorillonite minerals possess the added complication that they exhibit both intracrystalline and intercrystalline swelling and consequently the possibility of differences in behaviour between internal and external surfaces of the crystals has to be considered. Also the question as to whether the montmorillonite crystals in the dispersed state are broken up into unit lamellae which recondense to form crystals on drying, or in concentrated salt solutions, or whether the crystals retain their entity even in the dispersed state, has to be considered.

The structure of the dry montmorillonite cores appear from the nitrogen studies in Section 2 to be similiar to that of the Grundite illite in that the range of pore sizes extends to comparatively large pores in excess of 100 Å equivalent cylindrical radius. The shoulder on the desorption isotherm may also indicate relatively weak bonding forces between crystals. There is however, more evidence to indicate the stacking of crystals into domains if the second peak on the differential curve is regarded as arising from crystal separations within domains. If it is considered that the monovalent montmorillonite lamellae are unidispersed in suspension, the formation of crystals on drying may then be regarded as a particular case of domain formation as outlined in Section 3. The formation of one large single crystal by the whole montmorillonite clay mass on drying is probably prevented by the non-homogeneity of the mass and consequent mechanical interparticle friction and structural hindrances. Domains of these crystals (domains within domains) would be formed with the crystals fully swollen and on further drying, with the removal of the intracrystalline water, the crystals would contract resulting in the larger intradomainal spacings observed in the nitrogen studies.

On calcium saturating the suspension the crystals may be formed either immediately by the larger electrostatic attractive forces or the high salt concentration, or progressively on drying as for the sodium clay. In either case it appears from the smaller external surface area obtained that this statistical reformation of crystals is more effective for the divalent than for the monovalent clay.

From the maximum pore dimensions (approximately 50 Å) indicated by the point of divergence of the total volume - water content curves from the normal shrinkage line compared with those indicated by the nitrogen desorption isotherms (> 100 Å) and also the shape of the residual shrinkage line for the montmorillonite cores compared with those for the kaolinite and illite cores, it seems clear that the internal accommodation of intracrystalline swelling produces a considerable reduction in effective pore dimensions for the montmorillonite cores. The degree of this internal accommodation of intracrystalline swelling can be obtained from the difference between the total void volume of the clay cores and the volume of the adsorbed water equivalent to the adsorption of successive layers. With the adsorption of one layer of water molecules between each pair of lamellae the external surface may reasonably be assumed to have at least one layer of water molecules adsorbed on it. Similarly with the formation of the second and third internal layers the external surface probably has something like two and three layers adsorbed respectively.

From Table 23 it can be seen that with the formation of the first internal layer of water molecules the void volumes of the cores have increased from the oven dry values and an appreciable portion of the void volume is still unfilled. With the completion of the second internal layer however, the void volumes are approximately equal to the intracrystalline swelling plus the adsorption of two layers on the external surface. Similarly for the adsorption of three internal layers of water

# TABLE 23

## INTERNAL ACCOMMODATION OF INTRACRYSTALLINE SWELLING OF MONTMORILLONITES

| | | Equivalent water content (cc/100g) | Total volume of Clay from Experimentally Determined Relationship (cc/100g) | | | Extrapolated Real Volume of Clay (cc/100g) | Volume of Voids (cc/100g) | | | Oven Dry Porosity (cc/100g) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Exchangeable Cation | | | $Mg^{++}$ and $Ca^{++}$ | $Na^{+}$ | $K^{+}$ | | $Mg^{++}$ and $Ca^{++}$ | $Na^{+}$ | $K^{+}$ | $Mg^{++}$ and $Ca^{++}$ | $Na^{+}$ and $K^{+}$ |
| Clay | Number of Internal Water layers | | | | | | | | | | |
| Wyoming Bentonite | 1 | 11.9 | 55.5 | 54.0 | 52.0 | 37.5 | 18.0 | 16.5 | 14.5 | 13.5 | 10.4 |
| | 2 | 23.8 | 62.0 | 62.0 | 62.0 | " | 24.5 | 24.5 | 24.5 | | |
| | 3 | 35.9 | 73.0 | 73.0 | 73.0 | " | 35.5 | 35.5 | 35.5 | | |
| Redhill Montmorillonite | 1 | 12.9 | | 57.0 | | 37.5 | | 19.5 | | | 15.2 |
| | 2 | 25.8 | | 64.0 | | " | | 26.5 | | | |
| | 3 | 38.7 | | 75.3 | | " | | 37.8 | | | |

molecules plus the external contribution. From this it can be concluded that by the adsorption of the second internal layer, the pore volume of the montmorillonite clay cores has been completely filled by internal accommodation of this intracrystalline swelling. Consequently any further water uptake by these clays must arise either from an increase in film thickness or gel structure formation and not from an expansion of the initial oven dry porosity.

The difference in point of divergence from the normal shrinkage line between the sodium, calcium and magnesium Wyoming Bentonite cores and the potassium Wyoming Bentonite cores is undoubtedly associated with the difference in hydration energies of the ions and consequent differences in lattice spacings. From the data of Hendricks, Nelson and Alexander (1940) and Mooney, Keenan and Wood (1952), the d(001) spacing at pF 5.4 (0.80 relative vapour pressure) is approximately 15.5 Å for sodium, calcium and magnesium montmorillonite. For potassium montmorillonite, Hendricks, Nelson and Alexander (1940) obtained a diffuse 11.9 Å spacing between 0.70 and 0.90 relative vapour pressure. Hence it is possible that both the formation of pores by the collapse of intracrystalline spacings from a double water layer to a single water layer and unsaturation due to the proping apart of interlamellar spacings by the hydration sheels around the cations are responsible for the divergence from the normal shrinkage line. The former mechanism appears to be more effective in the potassium Wyoming Bentonite case and the second in the case of the remaining ions.

For Redhill montmorillonite the very much smaller crystal size and consequent larger volume of smaller pores may result in the earlier entry of air in terms of energy for the potassium ion (pF 5.3) than for the remaining ions (pF 5.6). These factors may also account for the absence of variation in water content on readsorption at high pF values between the two predrying procedures.

For the macroswelling monovalent montmorillonites it is obvious that if the crystal entity is retained on swelling without mechanical disturbance then the majority of the solution retained would be that actually associated directly with the surfaces of the clay lamellae. The measurement of repeat distances in excess of one hundred angstroms by Norrish (1954) for sodium montmorillonite supports this picture of crystal entity at least to quite high separations. The presence of hysteresis in the water content - suction relationship to low pF values for the monovalent clays and the variation between the different montmorillonites does however, indicate that other factors within the gel structure are also influencing solution uptake.

The film thicknesses on wetting the sodium montmorillonites to pF 1 with different electrolyte concentrations, calculated by dividing solution content by specific surface area are shown in Table 24. For solution concentrations of $\frac{N}{4}$ and less a total specific surface area of 760 $m^2/g$ was used. The values for N sodium chloride solution were obtained by dividing the solution content remaining after subtraction of that equivalent to a film thickness of 4.5 Å on the internal surfaces, by the external surface area of the crystals measured by nitrogen adsorption. For the additional montmorillonites the external surface areas used were those determined for the calcium clays and as pointed out for the Wyoming Bentonite, the sodium clay may have slightly different external surface areas.

## TABLE 24

## CALCULATED FILM THICKNESS AT pF 1 FOR MONTMORILLONITES ON SODIUM CHLORIDE SOLUTIONS

| | Calculated Film Thickness | | | | |
|---|---|---|---|---|---|
| Concentration | Distilled water | $\frac{N}{100}$ | $\frac{N}{10}$ | $\frac{N}{4}$ | N |
| Clay | | | | | |
| $Na^+$ Wyoming Bentonite | 249 | 100 | 64 | 47 | 131 |
| $Na^+$ Redhill Montmorillonite | 299 | 84 | 58 | 42 | 104 |
| $Na^+$ Maaza Montmorillonite | | 54 | 24 | 19 | 85 |
| $Na^+$ Panther Creek Montmorillonite | | 91 | 52 | 38 | 100 |
| $Na^+$ Tidinit Montmorillonite | | 91 | 49 | 25 | 64 |
| $Na^+$ Volclay Bentonite | | 119 | 80 | 63 | 189 |
| Theoretical | 400* | 114 | 48 | 33 | 19 |
| X-ray (Norrish) † | | 63 | 25 | 16 | 4.5 |

* Film thickness for $10^{-4}$ molar solution

† Free Solution

The film thicknesses calculated in this fashion for N sodium chloride solution are obviously unreasonable both from theoretical considerations and in comparison with those obtained for the more dilute concentrations. This gross overestimation can only be attributed to a considerable volume of solution enmeshed in a gel structure even if it were argued that some internal spacings may have expanded past the potential barrier at d(001) = 19 Å which seems unlikely. The measurement of a d(001) = 19 Å by X-ray techniques requires a minimum of about 5 lamellae per crystal. This means that the maximum external surface area consistent with such X-ray measurements is about 150 $m^2/g$. The film thicknesses on external surfaces for N sodium chloride solution calculated using this value would still be in excess of those obtained for $\frac{N}{4}$ using the total surface area of 760 $m^2/g$ thus supporting the above conclusion.

For the more dilute concentrations the variation between calculated film thicknesses for the various montmorillonites and the lack of agreement with diffuse double layer theory may arise from both gel formation and the existence of potential barriers. With the exception of the Maaza montmorillonite, for which the swelling is unduly restricted, the agreement with diffuse double layer theory improves with decreasing sodium chloride concentration to $\frac{N}{100}$. This agreement is however, qualitative rather than quantitative. The improvement may result from the internal accommodation of intracrystalline swelling within and consequent nullifying of the effect of the gel structure previously formed. Norrish (1954) found that between water contents of 37 cc/100g and 119 cc/100g for an oriented flake both 19 Å and 40 Å spacings were present but beyond 119 cc/100g the clay crystals were entirely expanded over the barrier. Since the solution contents involved at pF 1 for concentrations of $\frac{N}{4}$ and less are far greater than 119 cc/100g, the incomplete development of diffuse double layers may result simply from interparticle friction.

The film thicknesses calculated for the dialysed Wyoming Bentonite and Redhill montmorillonite on distilled water are very much less than those predicted for $10^{-4}$ N sodium chloride solution. From Schofield's (1946) calculations diffuse double layer theory appears to apply extremely well in very dilute solutions giving a slight overestimate of the actual measured film thickness. However the film thickness observed on lead glass after the addition of electrolyte tends to remain at about 500 Å for $\frac{N}{10}$ and greater concentrations whereas theory predicts a drop to about 60 Å for $\frac{N}{10}$ sodium chloride solution. The results of Bolt and Warkentin (1956) and Quirk (unpublished data) indicate that values very close to the correct surface area for sodium montmorillonite are obtained by measurement of the negative adsorption of chloride ions where the theoretical requirement is that the surfaces be separated by four times the calculated depth of exclusion of the chloride ions. Quirk (1957) has noted in fact that Schofield's $\frac{q}{n}$ gives a good estimate of the film thickness obtained by Norrish from his X-ray data. It may therefore be possible to explain this apparent discrepancy on the grounds that there is a second potential barrier at about 250 - 300 Å and that much higher spacings may be obtained on agitation in suspension than is indicated by X-ray measurements of oriented flakes in glass tubes or those developed in clay cores on slow wetting.

On the other hand if the film thicknesses measured by Norrish (1954) are those actually present in the cores the overestimation apparent in most cases could once again result from the additional solution enmeshed in the gel structure. It must be remembered of course that each spacing recorded by Norrish is in actual fact the mode of a distribution of spacings.

The observation by Kolaian (see Low, 1959) of an increase in water suction from near zero after stirring to an equilibrium value with time and the consequent transformation from a thick fluid to a thixotropic gel for an 11 per cent sodium bentonite suspension, could possibly be interpreted as arising from the development of a similiar gel structure as formed by the cores in the present work.

In Figure 81 the decrease in calculated film thickness for distilled water, $\frac{N}{100}$ and $\frac{N}{10}$ sodium chloride solution with increasing pF after wetting to pF 1 for sodium Wyoming Bentonite and Redhill montmorillonite are plotted in comparison with the theoretical diffuse double layer curves. For these concentrations there is a very approximate agreement between position and shape of the drying curves and those predicted by theory.

The X-ray observations of Norrish (1954) on the intracrystalline expansion of potassium montmorillonite with respect to the potential barrier appear to be very much in contrast with the present results. Norrish found that potassium montmorillonite having an initial spacing d(001) less than 15 Å did not swell beyond 15 Å as the concentration of electrolyte decreased. By saturating with sodium, expanding over the potential barrier and then leaching with dilute potassium chloride he found it was possible to obtain large spacings with potassium montmorillonite. On drying ,this clay showed no physical swelling and gave a maximum crystalline spacing of 15 Å on readsorption confirming the presence of potassium as the exchangeable cation. If the large swelling of the sodium montmorillonite is ascribed to large internal spacings it must be concluded that the potassium montmorillonite in the present work is also expanding internally to large spacings. The potassium cation does, however, appear to be less effective in pushing interlamellar spacings over the barrier and the degree of swelling is reduced compared with that for the sodium clays. It is important to note that the hysteresis for the potassium clays at pF values

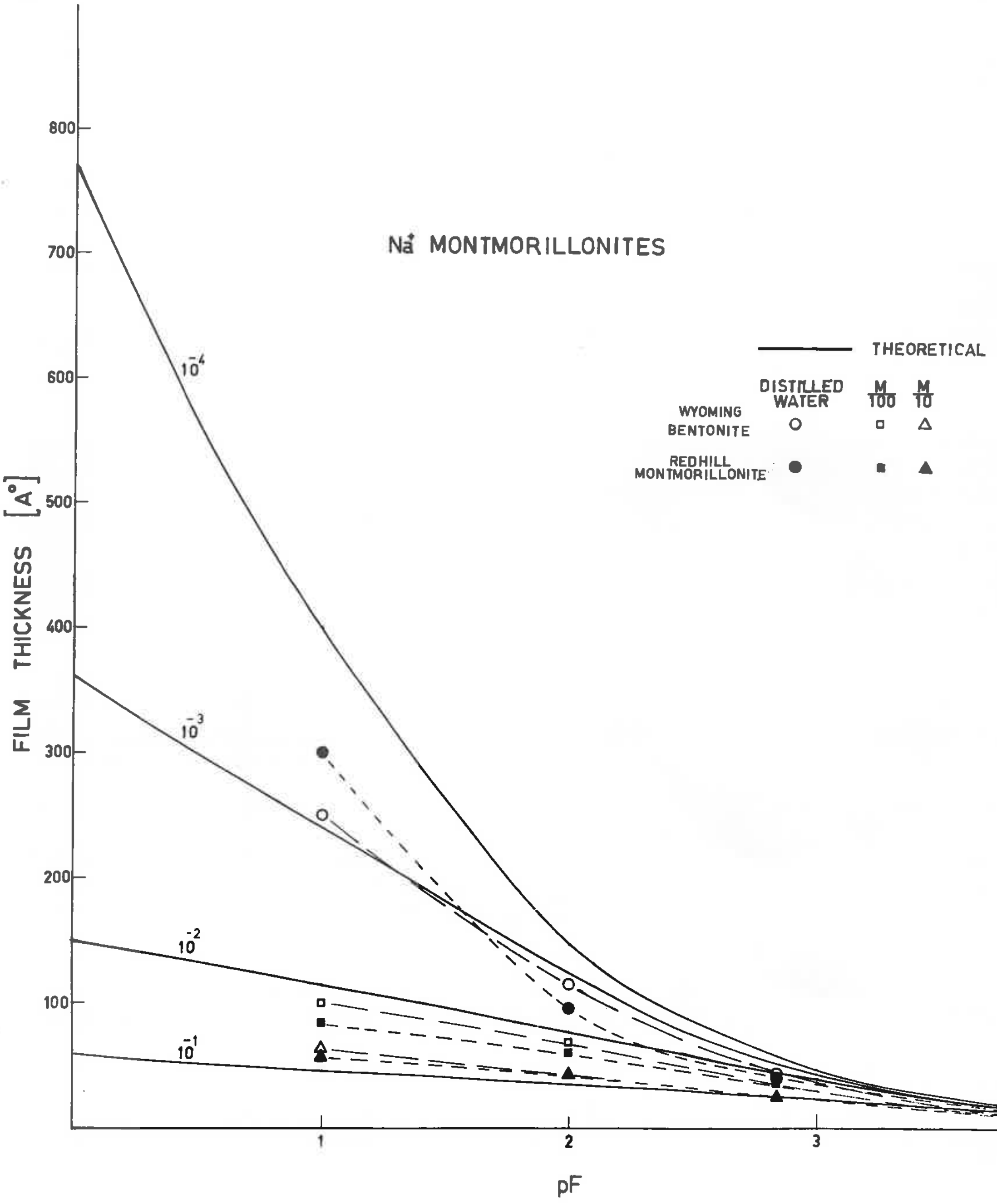

Na⁺ MONTMORILLONITES
THEORETICAL
DISTILLED WATER
M/100
M/10
WYOMING BENTONITE
○ □ △
REDHILL MONTMORILLONITE
● ■ ▲
$10^{-4}$
$10^{-3}$
$10^{-2}$
$10^{-1}$
FILM THICKNESS [A°]
800
700
600
500
400
300
200
100
1
2
3
4
pF

FIGURE 81.

below 4 is consistently greater than that for the sodium clays and may be due to a delay in expansion of many interlamellar spacings past the potential barrier even at very low pF values. At pF 2 an electrolyte concentration of $\frac{N}{10}$ appears to completely prevent the expansion of the potassium clay past the potential barrier. The non-expansion beyond 15 Å of the highly oriented flakes used by Norrish may therefore be less remarkable in view of the obviously delicate balance between attractive and repulsive forces at the limit of crystalline expansion for the potassium montmorillonite.

Calculation of film thickness on the external surfaces of the divalent calcium clays once again requires an allowance for the volume of solution adsorbed by crystalline swelling. The film thicknesses on the external surfaces on wetting to pF 1, obtained by subtracting the volume of solution equivalent to a d(001) = 15.4 Å for 4 M and d(001) = 19 Å for M and less concentrated solutions (Norrish, 1954) from the total solution content and then dividing by the nitrogen surface area, are shown in Table 25.

## TABLE 25

## CALCULATED FILM THICKNESS AT pF 1 FOR MONTMORILLONITES ON CALCIUM CHLORIDE SOLUTIONS

| | Calculated Film Thickness pF 1 (Å) | | | | |
|---|---|---|---|---|---|
| Concentration | Distilled water | $\frac{M}{100}$ | $\frac{M}{10}$ | M | 4M |
| Clay | | | | | |
| $Ca^{++}$ Wyoming Bentonite | 117 | 101 | 93 | 65 | 33 |
| $Ca^{++}$ Redhill Montmorillonite | 62 | 51 | 46 | 42 | 27 |
| $Ca^{++}$ Maaza Montmorillonite | 43 | 40 | 39 | 33 | 29 |
| $Ca^{++}$ Panther Creek Montmorillonite | 54 | 47 | 42 | 37 | 22 |
| $Ca^{++}$ Tidinit Montmorillonite | 34 | 33 | 31 | 28 | 22 |
| $Ca^{++}$ Volclay Bentonite | 129 | 119 | 103 | 69 | 28 |
| Theoretical | 200* | 57 | 24 | 10 | |

* $10^{-4}$ Calcium Chloride Solution

The situation is similiar to that for the normal sodium chloride solution in that the lack of agreement with theory and the wide variation between clays can only be taken as an indication of variations in gel forming properties of the clays. What is surprising however, is the magnitude of this gel formation at low pF values in solutions as strong as M and 4 M. These values are obviously excessive in terms of double layer formation and strongly suggest the possibility of a relaxation on wetting of a strained state existing for the dry clay matrix. The electron micrographs shown in Figures 25 to 30 indicate that the clay crystals in the dry clay matrix are subject to considerable distortion. Hence Terzaghi's (1927) idea of crystal bending on drying and subsequent relaxation on rewetting could be operative in increasing the solution uptake above that equivalent to surface film development and may account for the larger hysteresis observed at pF 2.84 for the M calcium chloride solution and the severe restriction to swelling in 4M. Both calcium illites (Figures 62 and 63) show a similiar increase in hysteresis at pF 2.84 with increasing electrolyte concentration. With the reduction in the electrostatic attractive forces as envisaged by MacEwan (1948) at separations of about 30 - 40 Å the elastic properties of the clay crystals may be sufficient to overcome the effective potential barrier and initiate the formation of gel structures. Once the structure has undergone this relaxation of mechanical strain the increase in suction necessary to cause a subsequent recompression of the structure, appears to be comparatively independant of the concentration of electrolyte present.

It may still be argued that diffuse double layer development for calcium montmorillonite systems could occur within such particle networks since the film thicknesses for a number of the calcium montmorillonites to concentrations as low as $\frac{M}{100}$ could be compatible with diffuse double layer theory. However, in every case the film thickness for distilled water is considerably less than diffuse double layer prediction. In addition the entry of chloride ions into intracrystalline spacings for $\frac{M}{10}$ and the relatively small exclusion from external surfaces even for $\frac{M}{100}$ calcium chloride solution seem to indicate little development of diffuse double layers.

The possibility of the values calculated for 4M being a genuine indication of film thickness on the external surfaces and not due to the formation of a gel structure cannot be overlooked. In this case some explanation other than diffuse double layer considerations is necessary to account for film thickness development at distances of approach of surfaces of the order of 30 - 40 Å.

## 2.4 Effect of Heating.

Following on the determination of specific surface areas and pore size distributions by means of the nitrogen adsorption apparatus, a number of the cores used in these determinations were rewet to low pF values to determine the effect of the strong desorption at $300^{\circ}C$ and $10^{-5}$ mm mercury pressure on the swelling characteristics of the clays. These preliminary observations indicated that whilst the montmorillonite clays were not significantly affected, the illite and to a lesser extent the kaolin clays showed appreciable reductions in swelling after this procedure. The reductions in swelling for the illites, particularly in the monovalent cases were quite dramatic, the water content at pF 1 of the sodium Willalooka illite cores being reduced from 841 cc/100g to 30.6 cc/100g, the cores remaining quite rigid, and that of the sodium Grundite illite cores being reduced from 131 cc/100g to 53.4 cc/100g.

In view of the possible association between this reduction in swelling after desorption and the degree of domain formation for these clays, further details of the effect of heating on Grundite and Willalooka illites and in addition the predominately illitic Urrbrae B clay were obtained. The natural Urrbrae B clay was saturated with various cations as previously described, washed with distilled water and filtered. The clay was not dialysed and no sand decantation was carried out.

### 2.4.1. Procedure.

After manufacture a number of cores of each of the clays saturated with various cations were placed in weighing bottles and the weight losses on heating to successively higher temperatures up to 400°C determined. Heating was carried out in an electric muffle furnace and weight losses determined after three days at each temperature by cooling the ground glass stoppered weighing bottles in a dessicator over phosphorus pentoxide powder and weighing.

The amounts of water readsorbed in equilibrium with 0.19 and 0.76 relative vapour pressure (pF 6.4 and 5.6) were determined by weighing to constant weight over the appropriate saturated salt solutions in dessicators.

Finally the cores were wet to pF 2 on the pressure plate apparatus and the water contents at equilibrium determined on the oven dry (110°C) basis.

### 2.4.2. Results and Discussion.

In Table 26 the decrease in weight of the clay cores between successive temperatures and 400°C has been expressed as a percentage on the basis of the weight of clay after drying to 400°C. The possible sources of weight loss on heating to increasing temperatures are surface adsorbed water, water of hydration of the exchangeable cations, hydroxonium ions in interlayer positions normally occupied by potassium ions in unweathered micas (Norrish and Brown, 1952) and hydroxyl groups from the clay lattice. Some weight loss may also occur from the charing of any organic matter present but this is probably insignificant for these materials. Surface adsorbed water is probably completely removed by 110°C corresponding to the large decreases in water content between room temperature (20°C) and

## TABLE 26

## WEIGHT LOSS BETWEEN SUCCESSIVE TEMPERATURES AND 400°C FOR ILLITES

| | Weight Loss (g/100g clay at 400°C) | | | |
|---|---|---|---|---|
| Temperature | 20°C | 110°C | 200°C | 300°C |
| Clay | | | | |
| Ca$^{++}$ Grundite | 7.19 | 2.09 | 1.31 | 0.68 |
| Mg$^{++}$ Grundite | 7.59 | 2.15 | 1.18 | 0.55 |
| Na$^{+}$ Grundite | 6.67 | 1.60 | 1.05 | 0.44 |
| K$^{+}$ Grundite | 6.01 | 1.57 | 1.11 | 0.60 |
| Ca$^{++}$ Willalooka | 16.39 | 4.92 | 2.47 | 1.22 |
| Mg$^{++}$ Willalooka | 21.07 | 4.82 | 2.36 | 1.20 |
| Na$^{+}$ Willalooka | 18.47 | 4.58 | 2.28 | 1.21 |
| K$^{+}$ Willalooka | 17.36 | 3.89 | 1.87 | 1.10 |
| Ca$^{++}$ Urrbrae B | 12.83 | 3.71 | 1.67 | 0.75 |
| Mg$^{++}$ Urrbrae B | 13.07 | 3.92 | 1.80 | 0.85 |
| Na$^{+}$ Urrbrae B | 13.47 | 3.27 | 1.58 | 0.80 |
| K$^{+}$ Urrbrae B | 11.27 | 3.24 | 1.53 | 0.73 |

110°C. In general the water contents from 110°C to higher temperatures show some relationship to the hydration energies of the exchangeable cations and the specific surface areas of the clays but the variation between different ions is not as large as might be expected if the water losses were entirely associated with exchangeable cations. Hence it seems possible that the loss of hydroxonium and hydroxyl ions are mainly responsible for the weight losses between 110°C and 400°C although the loss of hydroxyl groups from the crystal lattice has generally been considered to be very small at temperatures below 400°C.

In Tables 27 and 28 the water contents on rewetting to 0.19 and 0.76 relative vapour pressure respectively after heating to successive temperatures up to 400°C are shown. The water contents are again calculated on the basis of the weight of clay after drying to 400°C. The water losses at temperatures greater than 110°C appear to be permanent losses from the crystal lattice since they are not regained on readsorption and approximately the same differences between successive temperatures are maintained with increase in relative vapour pressure from 0.19 to 0.76. Decreases in B.E.T. surface areas calculated using water vapour adsorption data between unheated samples of an illite saturated with various cations and samples preheated to 600°C were attributed by Orchiston (1959) to decreases in hydrateable internal surfaces of the illite crystals. However, the X-ray data available on the illites used in the present work show no evidence to suggest that the interlamellar surfaces or cations are hydrated.

The water contents on wetting the cores to pF 2 after heating to successively higher temperatures up to 400°C calculated on the oven dry (110°C) basis are shown in Figures 82, 83 and 84 for Grundite illite, Willalooka illite and Urrbrae B clay respectively. At this low suction the differences due to the heating process between the clays and between the exchangeable cations become most apparent. For the divalent Grundite illite cores the heat treatment has little significant effect over the range of temperatures used. The monovalent cores, however, show an appreciable reduction in the water content at pF 2 with increasing temperature. On the other hand the divalent Willalooka illite and Urrbrae B clay cores

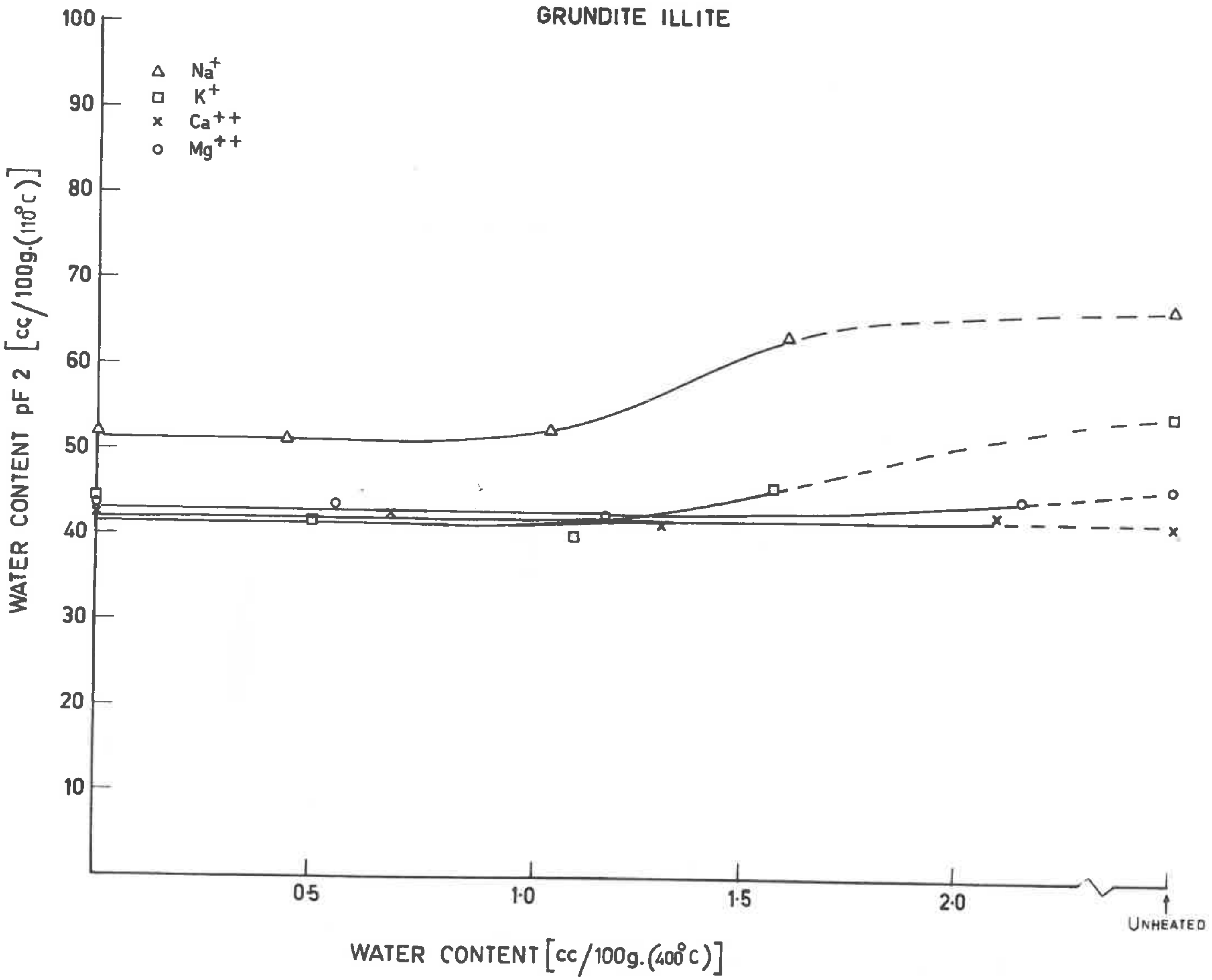

GRUNDITE ILLITE
△ Na⁺
□ K⁺
× Ca⁺⁺
○ Mg⁺⁺
WATER CONTENT pF 2 [cc/100g.(110°C)]
100
90
80
70
60
50
40
30
20
10
0·5
1·0
1·5
2·0
UNHEATED
WATER CONTENT [cc/100g.(400°C)]

FIGURE 82.

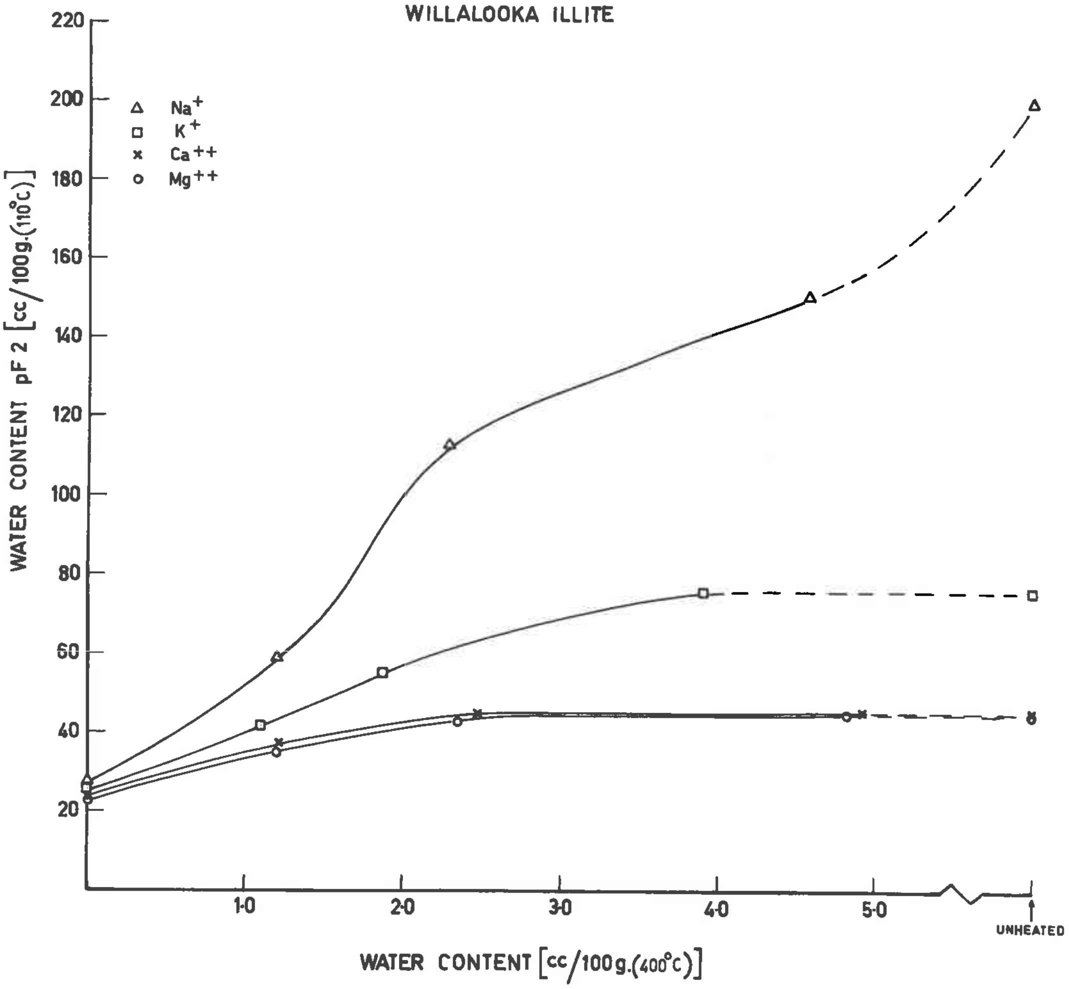

WILLALOOKA ILLITE
△ Na⁺
□ K⁺
× Ca⁺⁺
○ Mg⁺⁺
WATER CONTENT pF 2 [cc/100g.(110°C)]
220
200
180
160
140
120
100
80
60
40
20
1·0
2·0
3·0
4·0
5·0
UNHEATED
WATER CONTENT [cc/100g.(400°C)]

FIGURE 83.

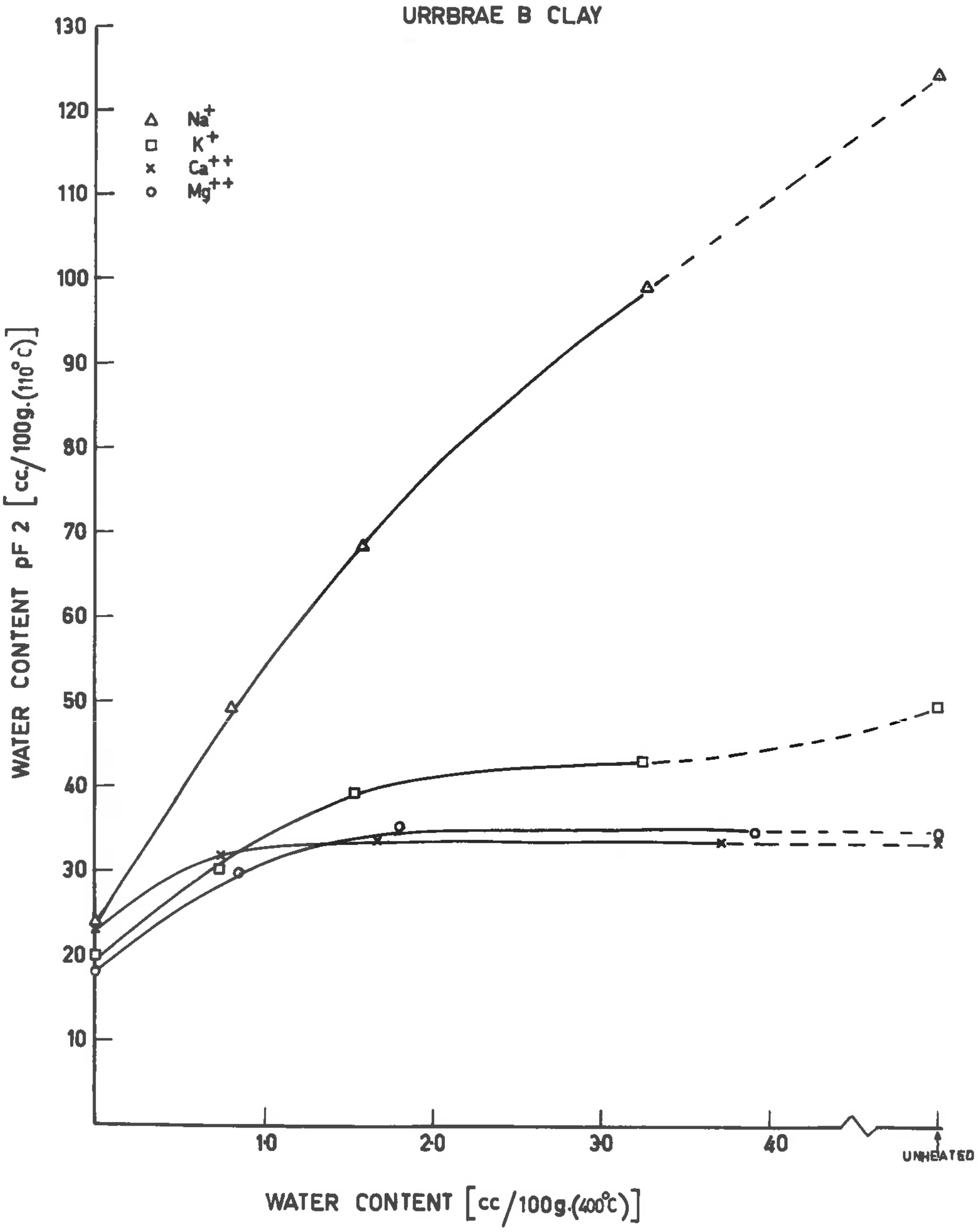

URRBRAE B CLAY
△ Na+
□ K+
× Ca++
○ Mg++
WATER CONTENT pF 2 [cc/100g.(110°C)]
130
120
110
100
90
80
70
60
50
40
30
20
10
1·0
2·0
3·0
4·0
UNHEATED
WATER CONTENT [cc/100g.(400°C)]

FIGURE 84.

## TABLE 27

## WATER CONTENT OF ILLITES ON REWETTING TO 0.19 RELATIVE VAPOUR PRESSURE AFTER PREHEATING TO VARIOUS TEMPERATURES

| | Water Content (g/100g clay at 400°C) | | | |
|---|---|---|---|---|
| Temperature | 110°C | 200°C | 300°C | 400°C |
| Clay | | | | |
| Ca$^{++}$ Grundite | 4.72 | 3.39 | 3.28 | 2.48 |
| Mg$^{++}$ Grundite | 5.39 | 3.95 | 3.30 | 2.43 |
| Na$^{+}$ Grundite | 3.87 | 2.83 | 2.64 | 2.01 |
| K$^{+}$ Grundite | 3.84 | 2.47 | 2.31 | 1.62 |
| Ca$^{++}$ Willalooka | 10.48 | 7.63 | 6.82 | 4.79 |
| Mg$^{++}$ Willalooka | 10.61 | 7.21 | 5.63 | 3.88 |
| Na$^{+}$ Willalooka | 9.50 | 7.27 | 5.68 | 4.10 |
| K$^{+}$ Willalooka | 8.18 | 6.28 | 5.35 | 4.20 |
| Ca$^{++}$ Urrbrae B | 7.36 | 4.54 | 2.95 | 2.91 |
| Mg$^{++}$ Urrbrae B | 7.47 | 4.32 | 3.37 | 2.60 |
| Na$^{+}$ Urrbrae B | 6.29 | 3.60 | 2.47 | 2.04 |
| K$^{+}$ Urrbrae B | 5.57 | 3.40 | 3.02 | 2.12 |

## TABLE 28

## WATER CONTENTS OF ILLITES ON REWETTING TO 0.76 RELATIVE VAPOUR PRESSURE AFTER PREHEATING TO VARIOUS TEMPERATURES

| | Water Content at 0.76 Relative Vapour Pressure (g/100g clay at 400°C) | | | |
|---|---|---|---|---|
| Temperature | 110°C | 200°C | 300°C | 400°C |
| Clay | | | | |
| $Ca^{++}$ Grundite | 10.83 | 8.86 | 8.46 | 7.55 |
| $Mg^{++}$ Grundite | 11.12 | 9.70 | 8.71 | 7.52 |
| $Na^{+}$ Grundite | 10.01 | 8.78 | 8.22 | 7.60 |
| $K^{+}$ Grundite | 8.99 | 7.56 | 7.43 | 6.87 |
| $Ca^{++}$ Willalooka | 22.35 | 19.78 | 18.55 | 16.23 |
| $Mg^{++}$ Willalooka | 22.86 | 19.65 | 17.97 | 15.52 |
| $Na^{+}$ Willalooka | 21.78 | 19.24 | 17.61 | 15.22 |
| $K^{+}$ Willalooka | 19.74 | 17.67 | 16.71 | 15.19 |
| $Ca^{++}$ Urrbrae B | 12.80 | 11.19 | 9.94 | 9.28 |
| $Mg^{++}$ Urrbrae B | 13.31 | 11.04 | 10.20 | 8.52 |
| $Na^{+}$ Urrbrae B | 12.97 | 10.64 | 9.40 | 8.26 |
| $K^{+}$ Urrbrae B | 11.44 | 9.38 | 9.20 | 8.16 |

although unaffected by preheating to 200°C show appreciable reductions in swelling after preheating to higher temperatures. The monovalent cores of these clays show a marked continuous reduction in swelling with increasing temperature. Since there appears to be a potential barrier determining the difference between the swelling of the monovalent and divalent cores of these clays, the preheating process even at relatively low temperatures appears to cause a progressive reduction in the ability of the monovalent clays to exceed this barrier.

The cause of these restrictions is not immediately apparent. Grim (1953) in reviewing the dehydration properties of illites obtained by numerous workers (Roy, 1948; Grim and Bradley, 1940, and Maegdefrau and Hofmann, 1937) indicates that there is no loss of structure even with the loss of hydroxyl groups until temperatures in excess of 850°C. In addition Brooks (1955) found that the surface area of an illite clay was essentially constant after the loss of surface adsorbed water and ion hydration water until temperatures in excess of 600°C were reached. Hence it seems very unlikely that any crystal deterioration has occurred in the present determinations.

The Willalocka illite and Urrbrae B clay again show differences in behaviour from that of the Grundite illite which may possibly indicate some connection between the degree of restriction to swelling on heating, and the degree of domain formation as indicated by the structural characteristics obtained earlier in this section. It is conceivable that the strong desorption could in some manner produce a partial or complete collapse in some spacings between parallel crystals within a domain. Partial collapse may result in sufficient increase in electrostatic attractive forces to prevent re-expansion. Complete collapse could prevent the rehydration of the exchangeable cations. However, no significant differences in exchange capacities could be detected between unheated samples of the clays and samples preheated to 400°C. The measured volumes of the cores were unchanged by the desorption at 300°C and $10^{-5}$ mm mercury pressure. In addition the volumes of liquid nitrogen adsorbed by the Willalooka illite and Urrbrae B clay cores at near saturation are very close to the oven dry (110°C) porosities of the cores indicating little structural collapse.

In these circumstances it appears that the restrictions must arise from a cementing action at areas of contact of individual crystals within domains thus preventing intradomainal expansion on rewetting. This could account for the greater restriction in the better oriented Willalooka and Urrbrae B clays and the small variations in swelling between exchangeable cations after heating to 400°C.

The greater surface density of charge for the illites and the possibility of increased hydrogen bonding in the kaolin clays may explain the appearance of this restriction after heating at relatively low temperature for these clays and the non appearance in the case of the montmorillonite clays.

# SECTION 5

## GENERAL DISCUSSION.

The fact that a tremendous variation in behaviour of clay-water systems exists between clay species and between individual members of the same clay species is very apparent from the results of this thesis. In addition it is obvious that mechanical particle to particle interaction and the formation of gel-like structures as represented in a simple fashion by Figure 32(b), can play a predominant role in determining the volume of solution retained by a clay mass at suctions below pF 4. These factors appear to be of paramount importance in drying from the suspension state but can also be important to a lesser extent in wetting from the dry state.

On drying from the suspension state large volumes of solution can be retained which are not directly associated with the clay surfaces but are simply enmeshed in a gel framework formed by the clay particles. In the majority of cases this factor prevents any satisfactory comparison between theoretical surface film thicknesses and those calculated from water content-suction data obtained in this fashion.

The reproducible hysteresis loops described on subsequent re-wetting and drying after drying a clay mass beyond its shrinkage limit, provide a better indication of the surface film development.

The evidence obtained from the nitrogen sorption isotherms and the electron micrographs indicates that in the dry state clay masses exist with varying degrees of particle orientation into groups which have been termed "domains". It is suggested that the formation of these domains of oriented crystals during the drying process, is produced by the requirements of osmotic equilibrium and the tendency to a state of minimum potential energy. This condensation into domains as outlined in Section 3 and also in a preliminary paper (Aylmore and Quirk, 1959) is considered to be a general phenomenon for all plate shaped clay minerals. The extent to which it occurs and the strength of the domains once formed being governed primarily by physico-chemical surface characteristics and structural considerations such as particle size and shape.

Irreversible hysteresis in clay-water systems (normal consolidation curve) and the difference in behaviour on shearing between consolidated and over-consolidated clays as observed by soil mechanics workers, can be explained in terms of this condensation process. Reversible hysteresis in the saturated state can on the other hand be considered to arise from the presence of a large number of independent domains in metastable states thus conforming to the domain theory of hysteresis as postulated by Everett and Whitton (1952). A combination of both phenomena undoubtedly occurs in the cases where large swelling and consequent rearrangement of the clay particles occurs on wetting from the dry state. When relatively little swelling occurs and also in the case of macrospores such as exist in natural aggregates, some consideration must be given to the additional solution absorbed due to an increase in volume of the pores within the clay matrix. For clay minerals with small particle size and a high degree of domain formation such considerations may be relatively unimportant. For the montmorillonite clay cores it has been shown that internal accommodation of intracrystalline swelling effectively removes that porosity not associated with separations between crystal faces.

In the oriented state it appears that potential barriers resulting from short range electrostatic attractive forces exist at close distances of approach. The surmounting of these barriers on the adsorption of solutions is determined largely by the valency of the exchangeable cations, surface density of charge and the concentration of electrolyte present. Domain behaviour is consequently characterized in general by restricted swelling in divalent systems or in high electrolyte concentration monovalent systems and large swelling in dilute monovalent systems.

Such behaviour is particularly well illustrated by the intracrystalline swelling of the montmorillonites and also by the Willalooka illite for which only intercrystalline swelling occurs. The montmorillonites occupy a special category since the low surface density of charge enables swelling to occur not only between crystals forming domains but also between the individual lamellae forming crystals. The crystals themselves may therefore be considered as particular types of domains if the individual lamellae are regarded as the basic units in swelling.

The illites exhibit differing degrees of domain behaviour, the Grundite illite with the highest surface density of charge and the largest particle size exhibiting less than the Urrbrae B clay and Willalooka illite.

The degree of domain formation for the kaolins is difficult to assess in view of the large crystal sizes and possible stepped nature of the crystal surfaces. However, it appears that the presence of additional attractive forces at low separations for these materials restricts swelling in the majority of cases.

In the dry state the surfaces of the crystals forming domains appear to be held at appreciable separations of about 30 Å or greater. The montmorillonite lamellae on the other hand return to essentially complete contact (d(001) = 9.6 Å) thereby excluding nitrogen adsorption, even after expansion to relatively large spacings. The larger intercrystalline spacings within domains must therefore arise from greater mechanical hindrances or else from the presence of repulsions which exist between surface charge distributions in the dry state. The latter repulsions may correspond to the potential barrier existing between 33 Å and 9 Å as observed for the intracrystalline swelling of the montmorillonites. It is conceivable that the drop back across this potential barrier which occurs for the montmorillonite lamellae in the saturated state, may be prevented from occuring for the larger crystals except at small areas of closest approach.

The restricted swelling of the divalent illites could therefore be explained as resulting either from a further potential barrier at approximately 60 Å separation as previously outlined (Section 4) or alternatively from the large electrostatic attractions at small areas below a potential barrier as above. The swelling of the illites (particularly the monovalent cores) has been shown to be markedly reduced by heating to relatively low temperatures ($< 400^{\circ}C$) at which little crystal deterioration is likely. A probable explanation of this phenomenon is that on the complete removal of water of hydration of the exchangeable cations, mica-like bonding occurs at the small areas of closest approach in the oriented state. Such areas must be very small since little surface area appears to be lost and also the exchange capacities of the clays are not significantly affected by the heating. The absence of such restrictions for the montmorillonite clays lends support to this bonding as the source of restriction since their surface density of charge is too low to prevent interlamellar expansion.

The simple domain model can only of course be considered an approximation to reality since the variation in size and shape and possible interleaving of the clay crystals as indicated by the electron micrographs must inevitably result in far more complicated systems.

A good deal of consideration has been given by many workers to the applicability of diffuse double layer formation to the swelling of clay-water systems. However, it should be remembered that such theories deal exclusively with repulsions and the film thicknesses predicted take no account of possible attractive forces arising from the presence of an opposing surface. MacEwan (1948) has suggested that electrostatic attractive forces will extend to at least 30 Å. From Norrish's results for the intracrystalline swelling of montmorillonite it appears that these electrostatic attractions extend to separations in excess of 100 Å. Consequently although diffuse double layer repulsions may exist the magnitude of the spacings developed may be appreciably lower than those predicted by this theory.

For the monovalent systems it seems likely that once the potential barrier within a domain has been overcome, the development of diffuse double layers as envisaged by the Gouy-Chapman theory plays a significant part in determining the solution uptake. Its applicability in a qualitative way is indicated by the marked effect of electrolyte concentration on the solution content of the sodium cores on wetting from the dry state. This sensitivity to electrolyte concentration is far less evident in drying from the suspension state as shown by the large solution contents retained in N sodium chloride solution. This seems to indicate that although diffuse double layers are present, their collapse with increasing electrolyte concentration takes place within the gel structure formed and hence does not give rise to an equivalent shrinkage. As diffuse double layer theory in a general way implies an equivalence between mechanical and osmotic components of the free energy, the existence of these gel structures is strongly supported by the sensitivity of the gels to increased mechanical pressure which induces particle rearrangement.

For divalent systems, however, the magnitude of the film thicknesses developed on wetting from the dry state and its insensitivity to variations in electrolyte concentrations less than M lead to the conclusion that swelling resulting from the formation of diffuse double layers does not become significantly operative in these circumstances. This is presumably because the strong electrostatic attractions prevent the expansion of the domain over the potential barrier. Where surfaces are not directly opposed it is possible that diffuse double layers do form but such formation appears to be of little significance in regard to divalent clay swelling. It might be argued that the lack of sensitivity to electrolyte concentration at the much higher solution contents obtained on drying from the suspension state could be attributed to the accommodation of diffuse double layers within the gel structure as for the sodium clays. However, there is no evidence to substantiate this suggestion and in view of the low values reported here and elsewhere (Quirk, 1957) for chloride exclusion from calcium systems such development seems unlikely.

The magnitude of the film thicknesses apparently developed in solutions as concentrated as M and 4 M where the condition of ideal solution required by diffuse double layer theory is certainly not fulfilled, seems to indicate that solution uptake is increased by a relaxation of structural strains within the clay matrix on lubrication by solutions. These strains may arise from the distortion of the crystal sheets in packing during the drying process. Such relaxations which appear to occur between pF 4 and 3 could possibly initiate the further development of gel structure.

In view of the obvious effect of the mechanical interaction between clay particles it must be concluded that before film thicknesses on clay surfaces can be estimated with accuracy from water content data the nature of the gel structure formation must be further clarified. The relevance of diffuse double layer concepts to divalent ion systems could be finally resolved by further detailed studies of chloride exclusion from such systems.

# SUMMARY

The hydration and swelling of a range of common clay minerals (kaolins, illites and montmorillonites) have been studied in relation to the clay species, specific surface area, exchangeable cation, electrolyte concentration and hydrostatic suction of the surrounding solution and the structural characteristics of the clay mass. This has been done using samples of the homoionic clays compressed at 1200 atmospheres pressure into small cylindrical cores to facilitate experimental determinations.

The specific surface areas of the clay cores were obtained and their structural status examined by the determination of low temperature nitrogen adsorption - desorption isotherms. Electron micrographs of fracture surfaces of the clay masses were also obtained. In the dry state varying degrees of parallel orientation of crystals with respect to each other have been shown to exist for the different clay minerals.

A simple model for the condensation of clay crystals on drying into oriented groups termed "domains" has been suggested and the effect of strong attractive forces, presumably electrostatic, within these domain structures on the swelling of the clays has been illustrated. The structural status of the clay mass and in particular the formation of gel-like structures has been shown to exert a considerable influence on the solution retention of clay masses.

In terms of theoretical considerations the formation of diffuse double layers appears to play a significant part in determining the swelling of monovalent systems but not in the case of divalent systems.

# ACKNOWLEDGEMENTS

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The author is grateful to Professor R. K. Morton for his encouragement and help and for permission to undertake this study within the Department of Agricultural Chemistry.

# APPENDIX 1

# CALIBRATION AND USE OF VOLUMETRIC NITROGEN ADSORPTION APPARATUS

## 1.1 Volume Calibration.

### 1.1.1. Gas Burette Volumes.

Values of the cumulative volumes from the reference mark of the gas burette to successive marks between the bulbs were 2.514, 5.380, 10.797, 16.437, 28.225, 39.859, 69.609 and 99.379 cc respectively. The volumes were obtained by direct calibration with mercury before joining the burette to the apparatus. Each value is the mean of several determinations and errors involved should be less than 0.005 cm$^3$.

### 1.1.2. Free Space Volumes.

For the low pressure manometer the volume of the free space varies with the pressure reading. The volume of the precision bore tubing was determined as 5.126 cc/cm; hence if $V_F$ is the free space at pressure Pmm and $V_F^o$ the free space at pressure $P = 0$.

$$V_F = V_F{}^o + 0.2563P$$

$V_F{}^o$ is determined by admitting a volume of gas to give a pressure reading of about 100 mm when the gas burette is filled with mercury. Pressure readings are taken when the mercury level in the gas burette is lowered to successive reference marks, then

$$\frac{PV_B}{T_B} + \frac{P(0.2563P)}{T_F} = \text{const.} - \frac{PV_F{}^o}{T_F}$$

where $V_B$ is the burette volume and $T_B$ and $T_F$ the burette and room temperatures respectively. Thus $-V_F^{\circ}$ is obtained as the gradient of a plot of the left hand side against $^{P}/T_F$.

The free space for the high pressure manometer used in conjunction with the cut-off is constant at any one temperature since the arms of the mercury in the cut-off are always returned to the same mark. In this case the equation becomes

$$\frac{PV_B}{T_B} = \text{const.} - \frac{PV_F^{\circ}}{T_F}$$

The free space is obtained as for the low pressure manometer by admitting a volume of gas to give approximately 700 mms pressure when the gas burette is filled with mercury and then lowering to successive reference marks. $V_F$ is then given by minus the gradient of a plot of the left hand side against $^{P}/T_F$ since

$$\frac{d\,\dfrac{PV_B}{T_B}}{d\,(^{P}/T_F)} = -V_F$$

### 1.1.3. Dead Space Volume.

On the assumption that helium is not adsorbed at liquid nitrogen (oxygen) temperatures, the dead space is determined by introducing a large quantity of helium into the gas burette-free space volume and calculating its volume $V_1$ at S.T.P. from known values of the free space, gas burette volumes and the observed temperature and pressure. On opening to the sample bulb at the temperature of the liquid nitrogen bath the pressure falls to

$P_2$ and $V_2$ cm$^3$ (S.T.P.) of gas remain in the gas burette - free space system.

If $V_D$ is the volume of the dead space,

$$V_1 - V_2 = V_D \times \frac{273}{T_D} \times \frac{P}{760}$$

During the determination of the nitrogen isotherm when there is pressure Pmm in the system and the dead space temperature $T_D$ the volume of nitrogen (S.T.P.) in the dead space $V_D$ (S.T.P.) is given by

$$V_D \text{ (S.T.P.)} = \beta_D \cdot \frac{P}{T_D} \left(1 + \frac{aP}{760}\right)$$

where $\beta_D = V_D \frac{273.2}{760}$ and a is a factor which allows for the deviation of nitrogen from the ideal gas laws, and equals 0.05 at 77.4°K and 0.0287 at 90.2°K.

## 1.2 Calculation of an Isotherm Point.

### 1.2.1. Volume of Nitrogen added to Gas Burette - Free Space System.

$V_B$ = 99.379cc $T_B$ = 298°K P = 286.75 mm

$\therefore$ $V_B$ (S.T.P.) $= 99.379 \times \frac{273}{298} \times \frac{286.75}{760} = 34.35$cc

$V_F$, calculated as in Appendix 1.1.2. = 4.48cc $T_F$ = 294°K

$\therefore$ $V_F$ (S.T.P.) $= 4.48 \times \frac{273}{294} \times \frac{286.75}{760} = 1.57$cc

$V_D = 0$

$\therefore$ Total Volume of Nitrogen (S.T.P.) = 34.35 + 1.57 + 0 = 35.92cc

### 1.2.2. On Opening to Sample Bulb at 78°K

$V_B$ = 99.379 cc  $T_B$ = 298°K  P = 122.10 mm

$$\therefore \; V_B \text{ (S.T.P.)} = 99.379 \times \frac{273}{298} \times \frac{122.10}{760} = 14.62 \text{ cc}$$

$$V_F\text{(S.T.P.)} = 4.48 \times \frac{273}{294} \times \frac{122.10}{760} = 0.67\text{cc}$$

$V_D$ (S.T.P.), calculated as in Appendix 1.1.3 = 2.33 cc

$\therefore$ Total Volume (S.T.P.) Unadsorbed = 14.62 + 0.67 + 2.33 = <u>17.62</u> cc

$\therefore$ Volume (S.T.P.) Adsorbed = 35.92 - 17.62 = <u>18.30</u> cc

Desorbed Weight of Sample = 1.7298g.

$$\therefore \text{ Volume (S.T.P.) Adsorbed per gram} = \frac{18.30}{1.7298} = 10.58 \text{ cc}$$

Measured Saturation Vapour Pressure = 769.9 mm

$$\therefore \text{ Relative Pressure } (P/P_o) = \frac{122.10}{769.9} = 0.159$$

i.e. 10.58 cc. (S.T.P.)/g. adsorbed at 0.159 relative pressure.

### 1.3 B.E.T. Plots and Surface Area Calculations.

The surface areas given in Table 3 were obtained from the B.E.T. plots reproduced in Figures 85 to 106.

$$\text{Intercept} = \frac{1}{v_m c} \qquad \text{Gradient} = \frac{1}{v_m} - \frac{1}{v_m c}$$

Hence $v_m$ per gram can be obtained

$$\text{Surface area per gram} = \frac{v_m \times 6.023 \times 10^{23} \times 16.2 \times 10^{-16} \times 10^{-7}}{22.4 \times 10^3}$$

since 22.4 litres at S.T.P. contains $6.023 \times 10^{23}$ molecules and packing area of nitrogen molecule = 16.2 Å$^2$ at 78° K

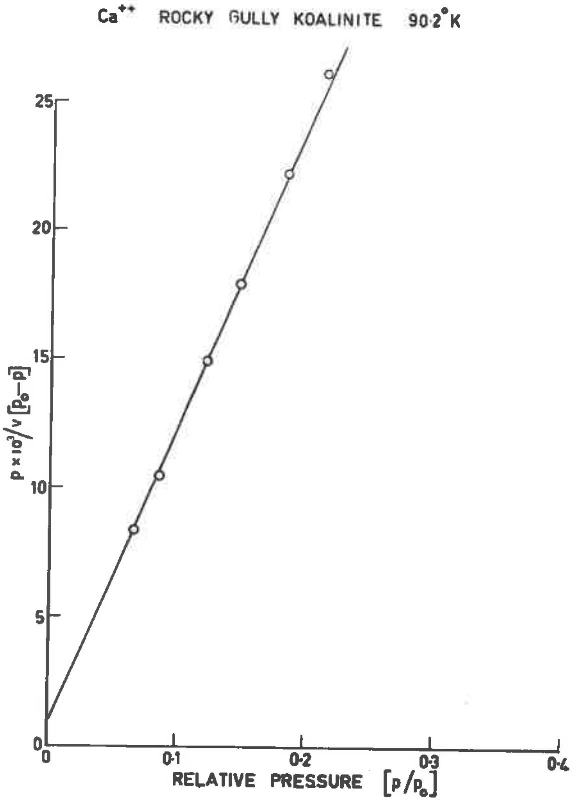

FIGURE 85.

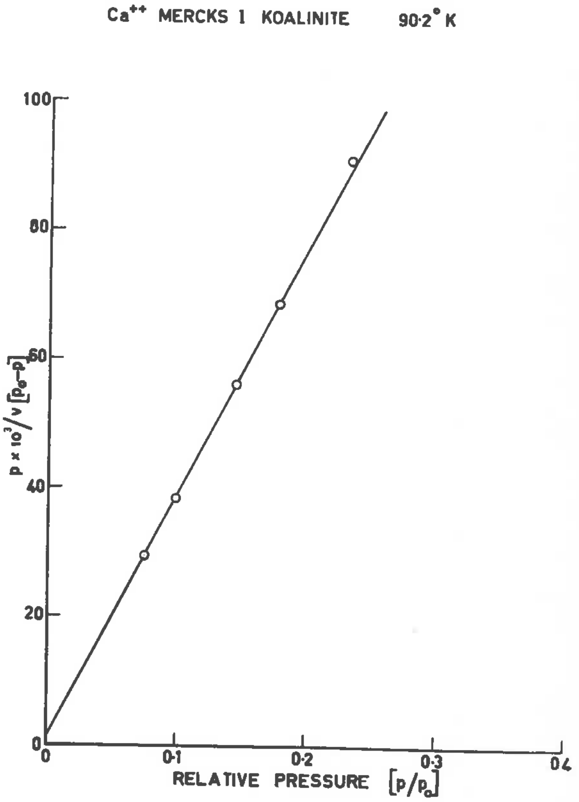

FIGURE 86.

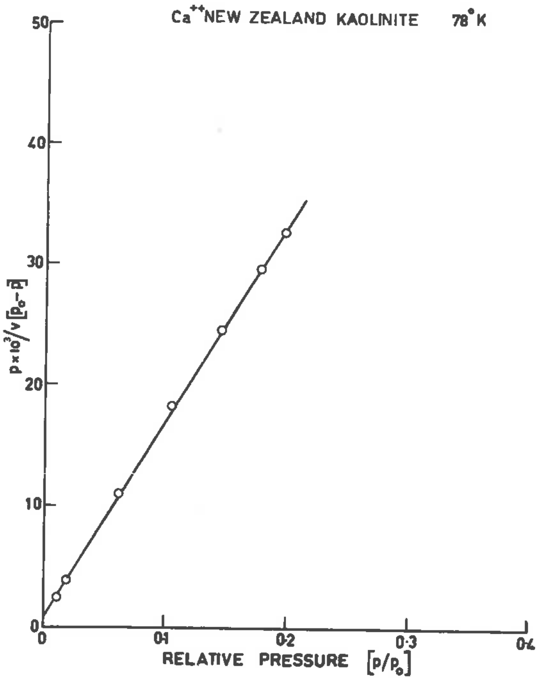

FIGURE 87.

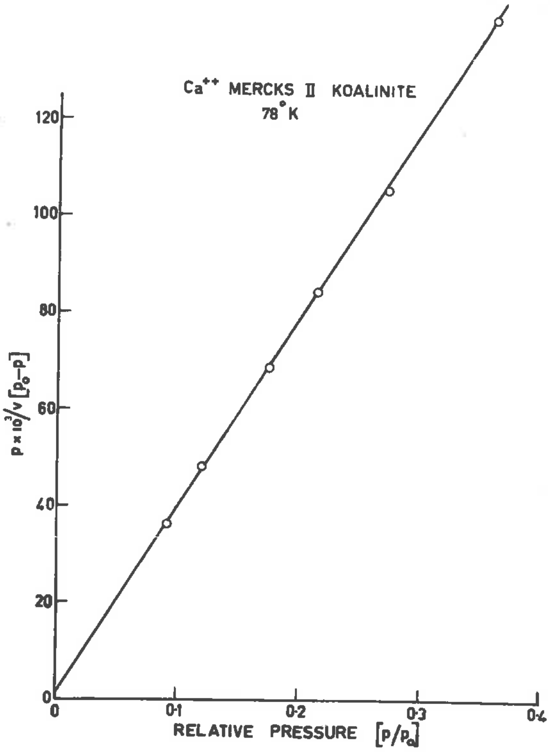

FIGURE 88.

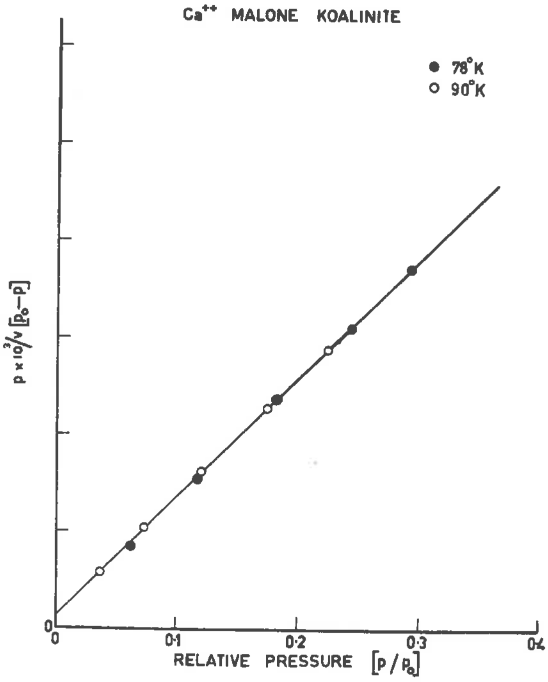

FIGURE 89.

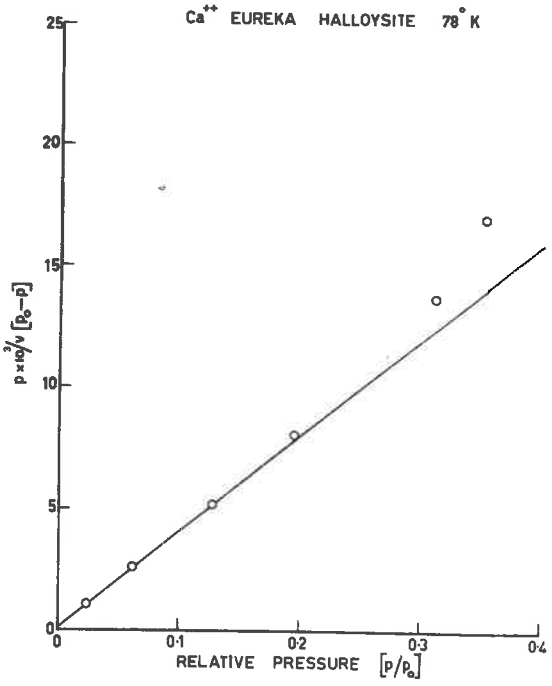

FIGURE 90.

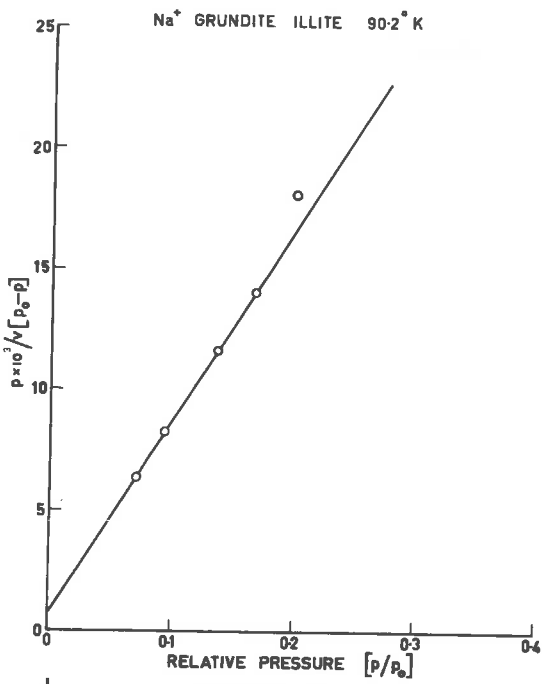

FIGURE 91.

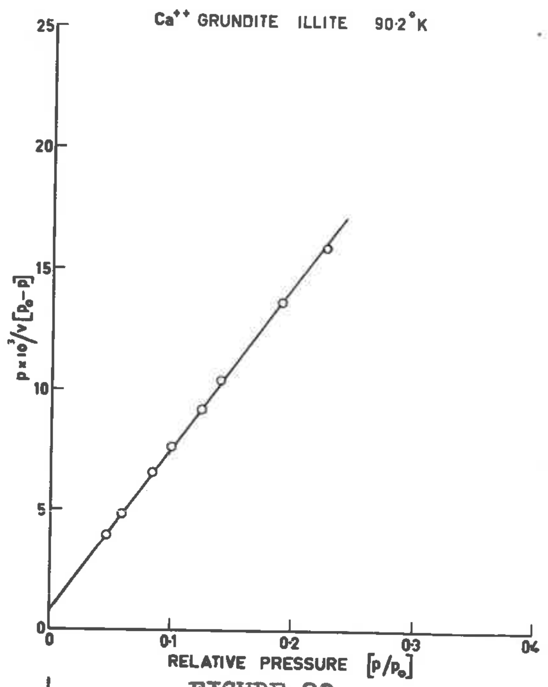

FIGURE 92.

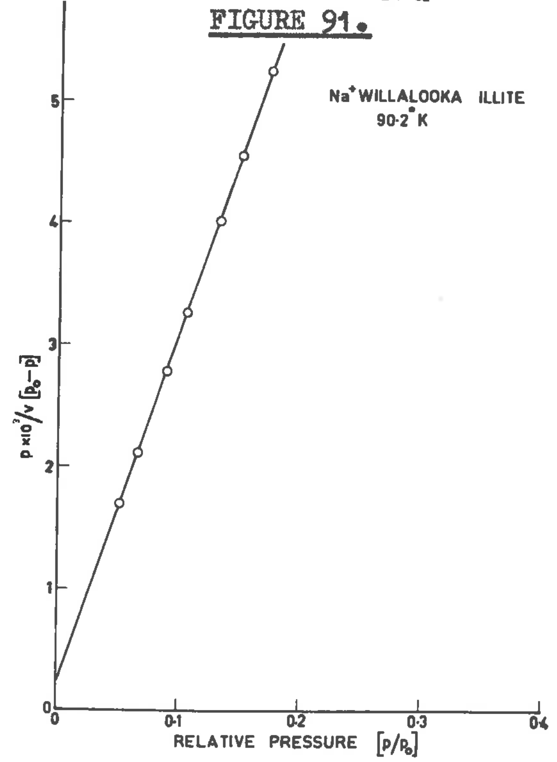

FIGURE 93.

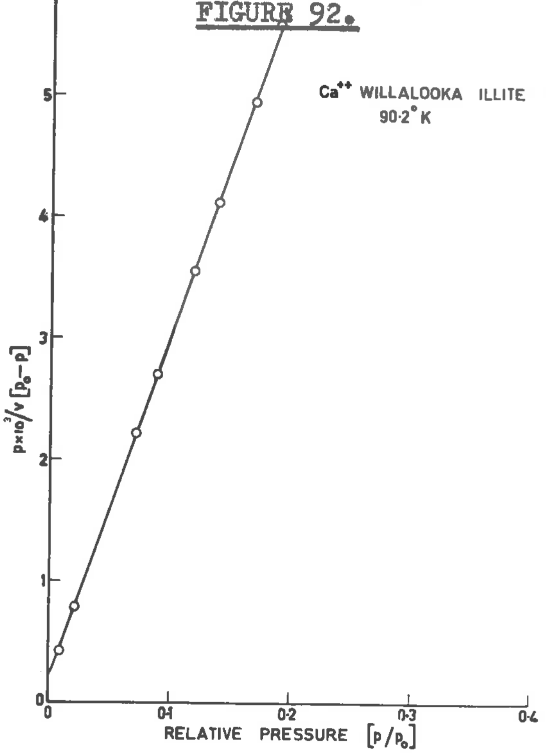

FIGURE 94.

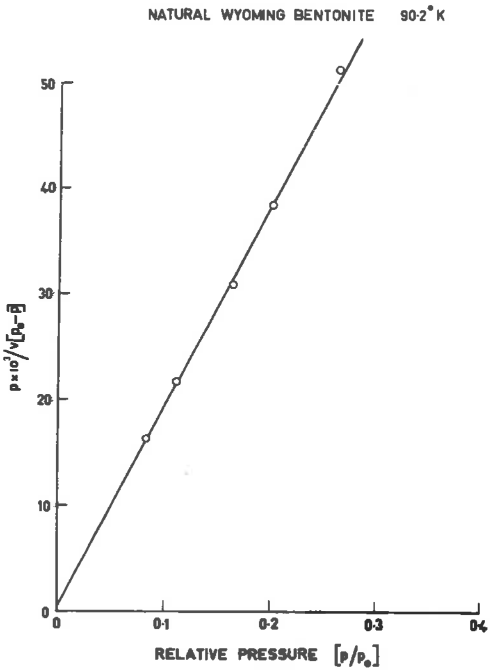

FIGURE 95.

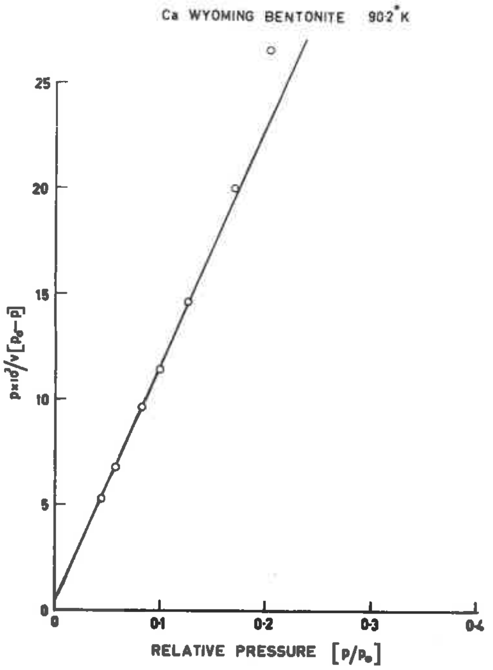

FIGURE 96.

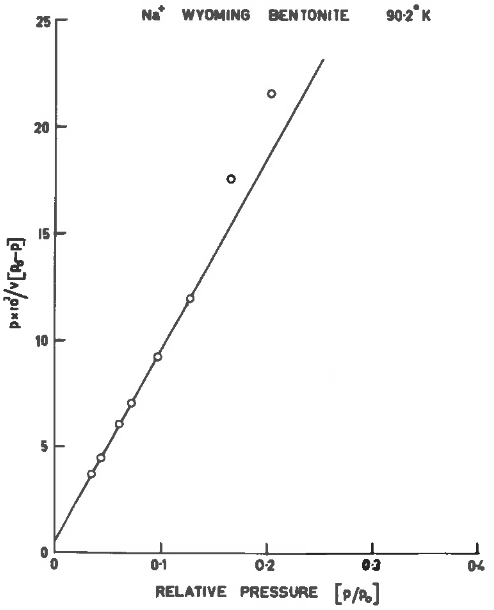

FIGURE 97.

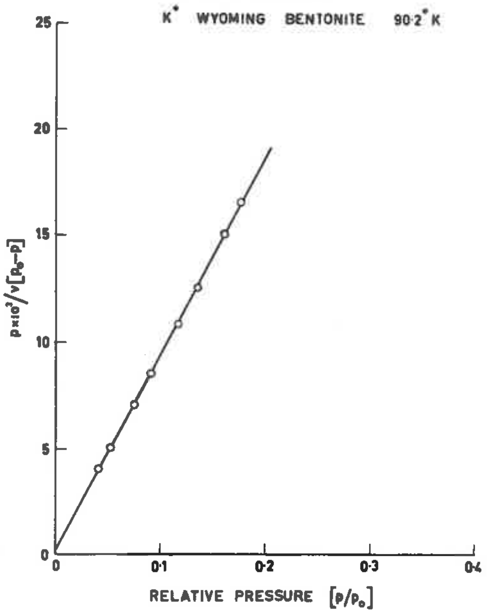

FIGURE 98.

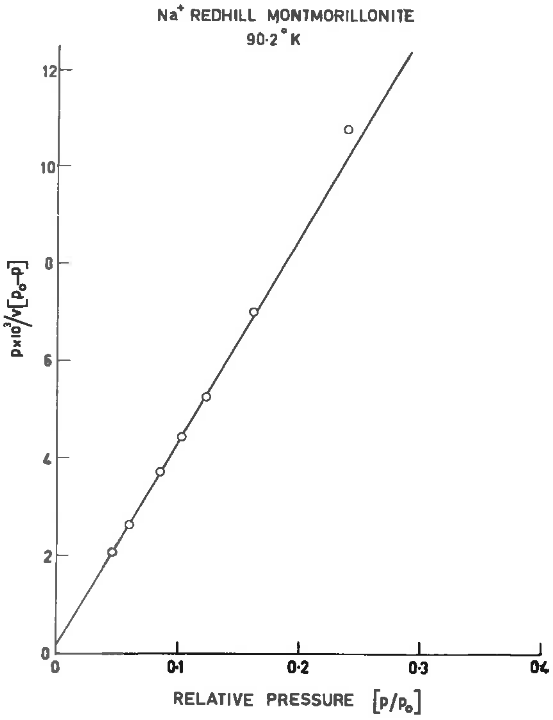

FIGURE 99.

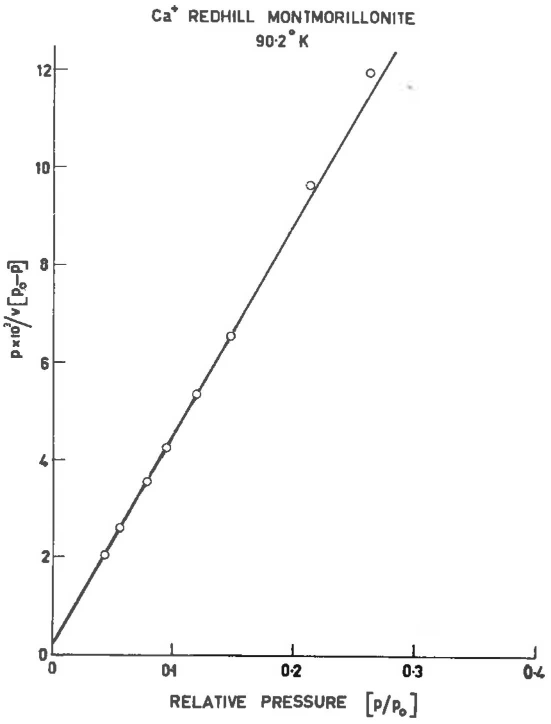

FIGURE 100.

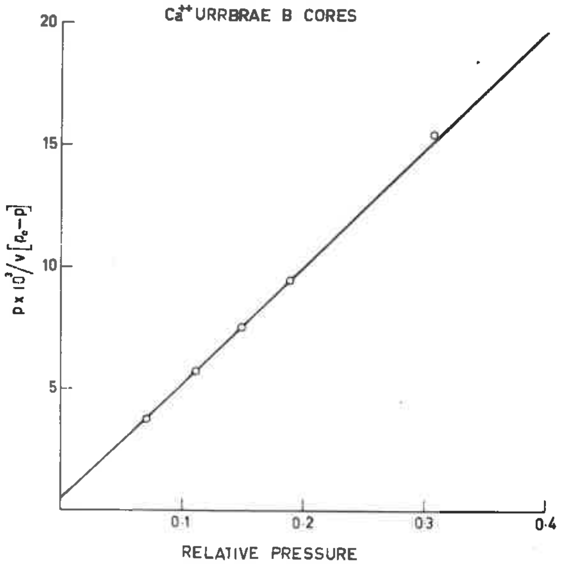

FIGURE 101.

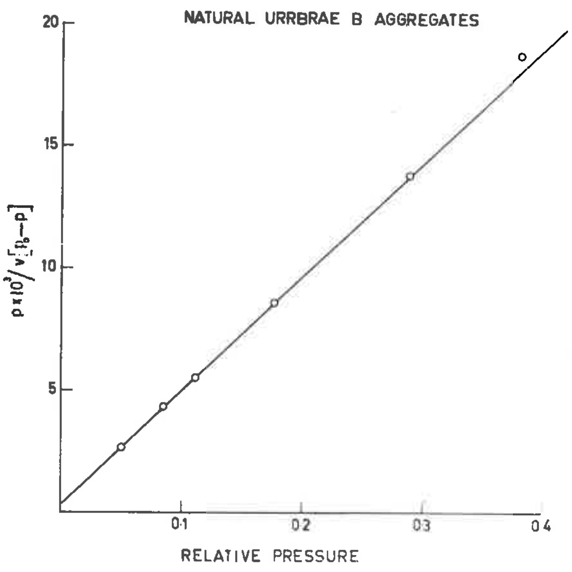

FIGURE 102.

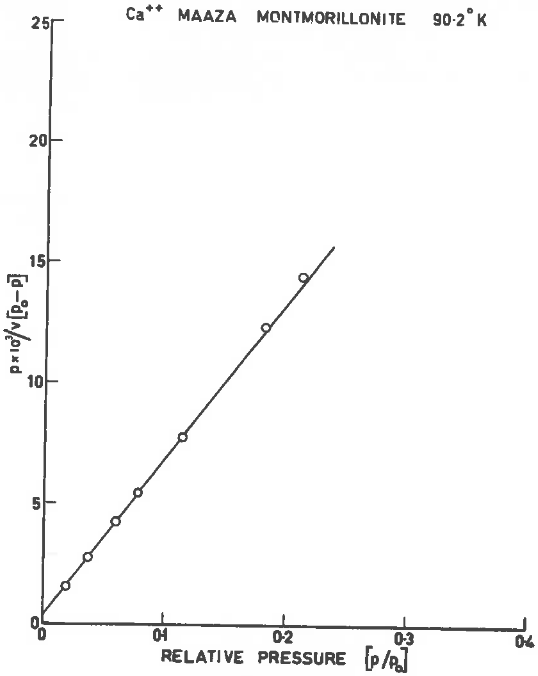

FIGURE 103.

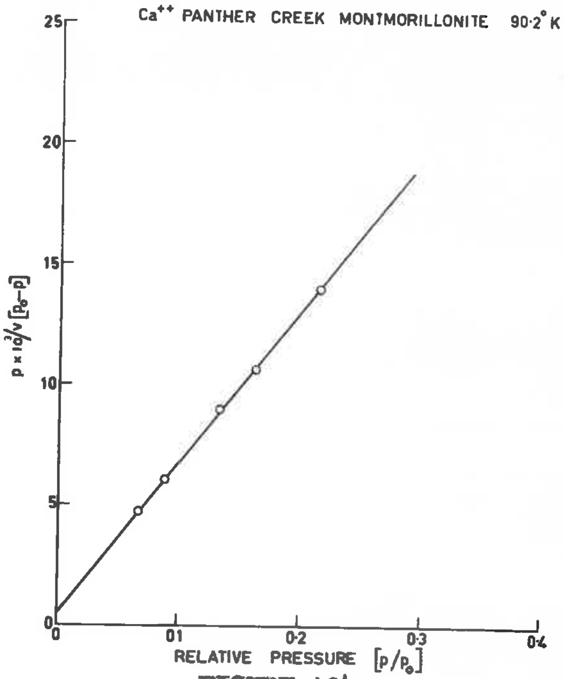

FIGURE 104.

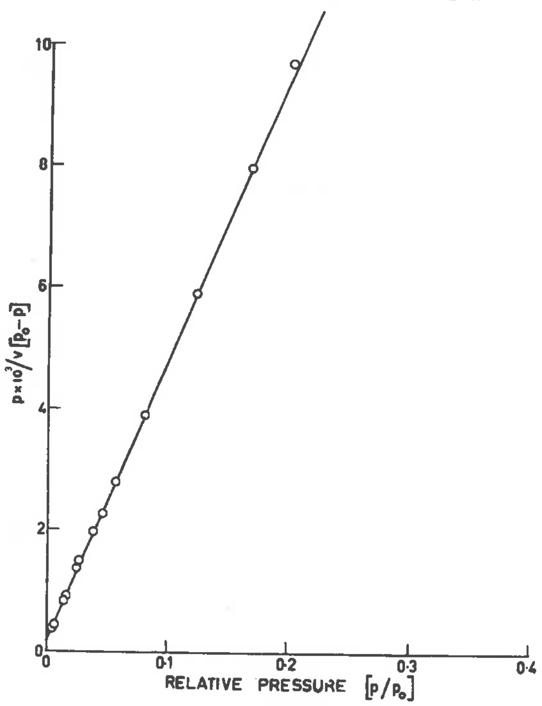

FIGURE 105.

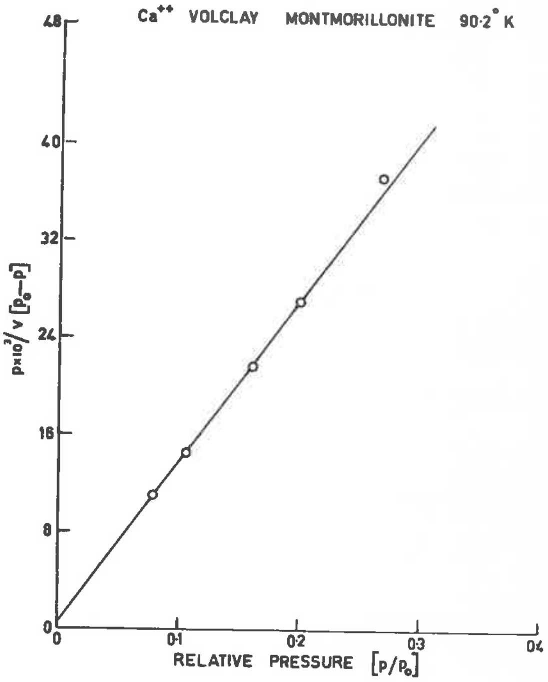

FIGURE 106.

## APPENDIX 2

## WATER VAPOUR SORPTION DATA FOR CORES OF SIX PRINCIPAL CLAYS

Except where indicated the adsorption data was obtained after predrying by evacuation over phosphorus pentoxide powder. The desorption data was obtained by drying from pF 1

### Rocky Gully Kaolinite

| | Water Content (cc/100g. clay (110°C)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cation | $Na^+$ | | $K^+$ | | $Ca^{++}$ | | $Mg^{++}$ | |
| Relative vapour Pressure | Wetting | Drying | Wetting | Drying | Wetting | Drying | Wetting | Drying |
| 0.96 | 18.0 | 20.0 | 18.0 | 21.3 | 18.4 | 20.5 | 18.1 | 19.9 |
| 0.76 | 3.0 | 3.1 | 2.9 | 3.1 | 3.2 | 3.7 | 3.3 | 3.8 |
| 0.51 | 1.6 | 1.9 | 1.8 | 2.0 | 2.2 | 2.5 | 2.1 | 2.5 |
| 0.32 | 1.0 | 1.3 | 1.3 | 1.4 | 1.6 | 1.8 | 1.4 | 1.6 |
| 0.19 | 0.8 | 0.8 | 1.0 | 1.0 | 1.2 | 1.3 | 0.9 | 1.3 |
| 0.10 | 0.7 | 0.7 | 0.6 | 0.7 | 0.6 | 0.8 | 0.7 | 0.9 |

**Mercks I Kaolinite**

| | Water Content (cc/100g. clay (110°C)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cation | Na$^+$ | | K$^+$ | | Ca$^{++}$ | | Mg$^{++}$ | |
| Relative vapour pressure | Wetting | Drying | Wetting | Drying | Wetting | Drying | Wetting | Drying |
| 0.96 | 10.4 | 14.4 | 7.5 | 10.7 | 8.0 | 10.0 | 8.0 | 9.3 |
| 0.76 | 2.0 | 2.2 | 1.3 | 1.5 | 1.9 | 2.1 | 1.9 | 2.2 |
| 0.51 | 1.1 | 1.3 | 0.7 | 0.9 | 1.4 | 1.6 | 1.4 | 1.6 |
| 0.32 | 0.8 | 0.9 | 0.6 | 0.7 | 1.1 | 1.3 | 1.1 | 1.0 |
| 0.19 | 0.4 | 0.5 | 0.4 | 0.5 | 0.8 | 0.8 | 0.8 | 0.8 |
| 0.10 | 0.4 | 0.5 | 0.2 | 0.2 | 0.3 | 0.5 | 0.6 | 0.7 |

<u>Grundite Illite</u>

| | Water Content (cc/100g. clay (110°C)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cation | $Na^+$ | | $K^+$ | | $Ca^{++}$ | | $Mg^{++}$ | |
| Relative vapour pressure | Wetting | Drying | Wetting | Drying | Wetting | Drying | Wetting | Drying |
| 0.96 | 17.6 | 21.1 | 15.2 | 17.7 | 15.5 | 17.9 | 16.1 | 18.0 |
| 0.76 | 7.3 | 10.0 | 6.2 | 8.0 | 7.5 | 9.8 | 7.7 | 9.8 |
| 0.51 | 4.0 | 6.0 | 3.5 | 4.7 | 4.8 | 6.5 | | 6.5 |
| 0.32 | 2.4 | 3.5 | 1.9 | 2.4 | 3.2 | 3.6 | 3.4 | 3.6 |
| 0.19 | 1.5 | 2.0 | 1.2 | 1.4 | 2.0 | 2.1 | 2.2 | 2.5 |
| 0.10 | 0.8 | 1.0 | 0.6 | 0.6 | 0.9 | 1.2 | 1.1 | 1.4 |

**Willalooka Illite**

| | Water Content (cc/100g. clay (110°C)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cation | $Na^+$ | | $K^+$ | | $Ca^{++}$ | | $Mg^{++}$ | |
| Relative vapour pressure | Wetting | Drying | Wetting | Drying | Wetting | Drying | Wetting | Drying |
| 0.96 | 30.9 | 37.9 | 27.9 | 33.0 | 26.5 | 30.2 | 26.3 | 30.4 |
| 0.76 | 17.8 | 23.7 | 15.5 | 21.0 | 16.8 | 20.6 | 16.9 | 20.7 |
| 0.51 | 11.2 | 13.5 | 8.7 | 10.5 | 11.0 | 13.7 | 11.3 | 13.8 |
| 0.32 | 6.7 | 7.8 | 5.1 | 6.3 | 7.4 | 8.1 | | 8.2 |
| 0.19 | 4.6 | 5.3 | 3.9 | 4.2 | 5.2 | 5.6 | 5.0 | 5.7 |
| 0.10 | 2.8 | 3.2 | 2.3 | 2.3 | 3.0 | 3.4 | 2.9 | 3.8 |

**Wyoming Bentonite**

| | Water Content (cc/100g. clay (110°C)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cation | Na$^+$ | | K$^+$ | | Ca$^{++}$ | | Mg$^{++}$ | |
| Relative Vapour Pressure | Wetting | Drying | Wetting | Drying | Wetting | Drying | Wetting | Drying |
| 0.96 | 38.2 (35.7) | 42.0 | 21.9 | 26.6 | 35.1 | 37.9 | 32.7 | 35.6 |
| 0.76 | 19.5 (16.2) | 21.7 | 10.6 | 14.1 | 20.5 | 21.7 | 19.4 | 20.8 |
| 0.51 | 13.3 (9.4) | 15.8 | 8.7 | 10.2 | 18.0 | 19.2 | 16.4 | 18.0 |
| 0.32 | 8.5 (5.7) | 11.0 | 5.7 | 7.6 | 13.8 | 15.7 | | 14.0 |
| 0.19 | 5.1 (1.5) | 8.0 | 3.5 | 4.9 | 9.3 | 10.5 | 9.6 | 10.2 |
| 0.10 | 3.1 (0.5) | 3.9 | 1.4 | 1.7 | 5.0 | 6.0 | 5.7 | 6.7 |

( ) Predried at 110°C

### Redhill Montmorillonite

| | Water Content (cc/100g. clay (110°C)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cation | $Na^+$ | | $K^+$ | | $Ca^{++}$ | | $Mg^{++}$ | |
| Relative vapour Pressure | Wetting | Drying | Wetting | Drying | Wetting | Drying | Wetting | Drying |
| 0.96 | 52.4 | 77.2 | 29.7 | 41.4 | 42.7 | 47.2 | 41.3 | 44.8 |
| 0.76 | 17.5 | 28.8 | 14.9 | 20.3 | 25.0 | 27.4 | 24.0 | 26.1 |
| 0.51 | 12.0 | 20.9 | 10.0 | 14.5 | 20.2 | 22.7 | 18.3 | 20.7 |
| 0.32 | 6.8 | 12.6 | 6.6 | 8.3 | 14.2 | 17.0 | 13.8 | 15.7 |
| 0.19 | 3.5 | 9.0 | 3.5 | 4.9 | 11.5 | 12.6 | 9.0 | 11.1 |
| 0.10 | 1.5 | 3.5 | 1.6 | 1.6 | 6.5 | 8.0 | 5.4 | 7.8 |

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