Royal Society of Chemistry
PAPERBACKS

ION EXCHANGE:
Theory and Practice

2nd Edition

C.E. Harland

ION EXCHANGE

Theory and Practice

Second Edition

Royal Society of Chemistry Paperbacks

Royal Society of Chemistry Paperbacks are a series of inexpensive texts suitable for teachers and students and give a clear, readable introduction to selected topics in chemistry. They should also appeal to the general chemist. For further information on selected titles contact:

Sales and Promotion Department
The Royal Society of Chemistry
Thomas Graham House
The Science Park
Milton Road
Cambridge CB4 4WF, UK

Titles Available

Water *by Felix Franks*
Analysis – What Analytical Chemists Do *by Julian Tyson*
Basic Principles of Colloid Science *by D. H. Everett*
Food – The Chemistry of Its Components (Second Edition)
by T. P. Coultate
The Chemistry of Polymers *by J. W. Nicholson*
Vitamin C – Its Chemistry and Biochemistry
by M. B. Davies, J. Austin, and D. A. Partridge
The Chemistry and Physics of Coatings
edited by A. R. Marrion
Ion Exchange: Theory and Practice, Second Edition
by C. E. Harland

How to Obtain RSC Paperbacks

Existing titles may be obtained from the address below. Future titles may be obtained immediately on publication by placing a standing order for RSC Paperbacks. All orders should be addressed to:

The Royal Society of Chemistry
Turpin Distribution Services Limited
Blackhorse Road
Letchworth
Herts SG6 1HN, UK

Telephone: +44 (0) 462 672555
Fax: +44 (0) 462 480947

Royal Society of Chemistry Paperbacks

ION EXCHANGE

Theory and Practice

Second Edition

C. E. HARLAND

The Permutit Company Limited
(Part of Thames Water plc), UK

ROYAL
SOCIETY OF
CHEMISTRY

ISBN 0-85186-484-8

A catalogue record for this book is available from the British Library

Published by The Royal Society of Chemistry,
Thomas Graham House, The Science Park,
Milton Road, Cambridge CB4 4WF, UK

Typeset by Keytec Typesetting Ltd, Bridport, Dorset
Printed in Great Britain by The Bath Press, Lower Bristol Road, Bath

Preface

AIMS

This publication is a revision of the first edition issued in 1975, as part of the then Chemical Society's highly successful 'Monographs for Teachers' series. Many significant advances have been made during the intervening years with regard to process development, ion exchange materials, equipment engineering, and the continuing quest for a better understanding of fundamental principles.

The 1990s see the realization of over fifty years growth in the principal application of ion exchange; therefore the aims and objectives of this revision are deliberately somewhat different from the earlier edition. The salient material concerning the early history of the subject is retained, but in dealing with modern developments more emphasis is placed on the properties of modern resins and the interrelationship between processes and fundamental theory. In this way it is hoped to sacrifice a formal catalogued review approach in favour of cultivating interest and better understanding. Ion exchange using modern exchangers is an excellent vehicle for experimentation and demonstration of not only key topics in a school's core curriculum science syllabus, but also as a possible component of student project investigations into any one of a host of electrolyte solution chemistry topics. In order to support an interest in the latter, simplified procedures for characterizing organic exchangers and selected bench experiments have been included in separately identified text (**Boxes**), but it is also hoped that, within teaching institutions, students will be encouraged to recognize the potential use of ion exchangers in their own experimental and project programmes (see Note 1).

In industry, not all personnel responsible for either purchasing or operating ion exchange plant have necessarily been formally versed in the mysteries of the subject. With this fact in mind this paperback, within the constraints imposed by length, sets out to explain the principal elements concerning exchanger characteristics, fundamental theory, and key process applications. It remains the prerogative of reviewers and readers to decide how well the author's stated aims have been met to produce an informative paperback which complements the more rigorous and comprehensive texts currently available.

An exhaustive literature review is purposely not included, but instead, principal subject categories are referred to a bibliography by chapter listing authoritative texts and publications by which means a more detailed study of a topic and access to the formal scientific literature may be accomplished.

THE SUBJECT

Observations of the phenomenon of ion exchange date from ancient times. The 'mechanism' of the reaction, however, was established in 1850 by two English chemists, H. S. Thompson and J. T. Way, but it is only in the past few decades that the subject has expanded to become a true science from which extensive industrial applications have emerged. Progress in both the theoretical understanding and process developments of ion exchange has been rapid with the one complementing the other. In the academic sphere, the growth of knowledge has paralleled closely the physical chemistry interpretation of the behaviour of concentrated solutions of electrolytes. This is not unexpected since ion exchange materials are in effect electrolytes, albeit mostly solid ones, and in some respects they behave in an identical fashion. Undoubtedly, present day inadequacies in the theory and understanding of certain aspects of ion exchange stem from the lack of knowledge and precise interpretation of the various forces and effects of electrical origin which govern the chemical behaviour of electrolyte solutions.

The scale and scope of industrial ion exchange has grown enormously since the early days of water softening, through which the subject achieved worldwide acclaim. Water treatment is still the largest single industrial application of ion exchange, and at present there is a large and increasing demand not only for softened water, but also for 'pure' or demineralized water. Vast amounts of such high quality water are essential to many highly technological industries such as those producing fabricated metals, paper, synthetic fibres, electronic components, processed foodstuffs, pharmaceuticals, and electrical power. Much current research and process development is directed towards utilizing ion exchange methods for obtaining potable water from sources which in one way or another fail to meet current European Union (EU – formerly European Community or EC) directives, for example high nitrate levels or excessive salinity.

'Matter may be neither created nor destroyed' but, if no one is looking, it may be thrown away. However, people are looking and the public awareness of a need to control effluent disposal, and so reduce environmental pollution, has never been higher. The practice of ion exchange in the field of effluent treatment is well established, and its potential uses in these areas with the added advantage of reagent recovery and water re-use are always under active review.

In many mineral fields it is becoming increasingly apparent that, although the demand for growth increases, the natural resources and quality of raw materials are decreasing. This is particularly true in many aspects of extraction metallurgy where good quality ore bodies are being rapidly depleted and man is being compelled to utilize lower grade materials which frequently demand new and more efficient processing techniques. It is in many such applications that ion exchange has proved extremely useful and it is to be expected that the techniques will be used on an ever-increasing scale in the future.

In medicine, also, considerable use is being made of ion exchangers, particularly in the production of water to meet the stringent quality specification required for pharmaceutical and cosmetic formulations. The controlled, slow release of drugs and other chemicals into the body has also been made possible by means of these versatile components.

The earliest references to ion exchange are in relation to soils and fertility. It may not be surprising, therefore, that modern synthetic exchangers have wide potential application in agriculture and horticulture. Elements vital to plant growth may be introduced to soils and other fertile media by means of ion exchangers, from which they may be liberated at a controllable rate.

Finally, any preface to the subject of ion exchange cannot omit to highlight the impact made by ion exchange chromatography; not only historically through its firstly being responsible for the separation of chemically similar species such as the lanthanides, actinides, and amino acids, but also the more recent achievement whereby micro-quantities of ion mixtures may be rapidly separated and individual components quantitatively detected at sub-microgram levels.

Note 1

BOXES describing experiments and demonstrations may be read separately from the main text, and the following identities apply where appropriate:

ml ≡ cm^3
%, or %w/v ≡ grams per 100 cm^3 solvent
normality, N ≡ g equiv. l^{-1}
BV ≡ 'tapped down' bed volume
SAC ≡ strong acid cation resin
WAC ≡ weak acid cation resin
SBA ≡ strong base anion resin
WBA ≡ weak base anion resin

Where an estimated time is stated it is assumed that standard reagents, resins in the appropriate ionic form, and all other equipment items are immediately available. Where deionized water is specified, distilled water may be used as an alternative. Where methyl orange indicator is stated, BDH 4.5 indicator may be substituted if preferred.

Contents

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

Some Basic Principles of Industrial Practice 166

Chapter 8

Water Treatment 179

Chapter 9

Non-water Treatment Practices 238

Chapter 10

Boxes

Acknowledgements

I would like to gratefully acknowledge the valuable assistance and encouragement given by family, friends, and colleagues towards the production of this book.

Firstly I would like to thank my family, and especially my wife Helen, for their support and encouragement.

I thank my friends and colleagues within The Permutit Company Ltd and PWT Projects for their technical assistance and patience whilst proofreading, and the Permutit Company Ltd for their permission to publish.

A special appreciation is extended to Denise Pearsall for her enthusiasm, devotion to the task, and patience whilst typing the draft copy. I thank also Mr Norman Robertson for his computer drafting of tabulated material.

C. E. Harland

October 1993

Chapter 1

Discovery and Structure of Solid Inorganic Ion Exchange Materials

THE PHENOMENON

An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase, the ion exchanger being insoluble in the medium in which the exchange is carried out. If an ion exchanger M^-A^+, carrying cations A^+ as the exchanger ions, is placed in an aqueous solution phase containing B^+ cations, an ion exchange reaction takes place which may be represented by the following equation:*

$$\underset{\text{Solid}}{M^-A^+} + \underset{\text{Solution}}{B^+} \rightleftharpoons \underset{\text{Solid}}{M^-B^+} + \underset{\text{Solution}}{A^+} \tag{1.1}$$

For reasons which will be considered later, the anion in solution does not necessarily take part in the exchange to any appreciable extent. The equilibrium represented by the above equation is an example of *cation exchange*, where M^- is the insoluble fixed anionic complement of the ion exchanger M^-A^+, often called simply the *fixed anion*. The cations A^+ and B^+ are referred to as *counter-ions*, whilst ions in the solution which bear the same charge as the fixed anion of the exchanger are called *co-ions*. In much the same way, anions can be exchanged provided that an anion-receptive medium is employed. An analogous representation of an *anion exchange* reaction may be written:

$$\underset{\text{Solid}}{M^+A^-} + \underset{\text{Solution}}{B^-} \rightleftharpoons \underset{\text{Solid}}{M^+B^-} + \underset{\text{Solution}}{A^-} \tag{1.2}$$

---

* An ion may be defined as an atom or combination of atoms (molecule) which carry a net positive (cation) or net negative (anion) electrical charge.

Further development of a physical model for the exchanger phase is best left until Chapter 2 when synthetic ion exchangers will be considered in more detail, but the previous equations illustrate the essential difference between ion exchange and other sorption phenomena. The main fact is that electroneutrality is preserved at all times in both the exchanger and solution phases, and this in turn requires that counter-ions are exchanged in *equivalent* amounts. The most important features characterizing an ideal exchanger are:

1. A hydrophilic structure of regular and reproducible form.
2. Controlled and effective ion exchange capacity.
3. Rapid rate of exchange.
4. Chemical stability.
5. Physical stability in terms of mechanical strength and resistance to attrition.
6. Consistent particle size and effective surface area compatible with the hydraulic design requirements for large scale plant.

Manufacturers of modern ion exchange materials have progressed a long way towards meeting all these requirements when compared with the prototype materials described below. The cost to industry of modern ion exchange resins is high, varying typically from £1000 to £4000 per m^3. Therefore exchanger properties which minimize the volumes required (*e.g.* high exchange capacity), or which prolong resin life (*e.g.* physical and chemical stability), are important considerations. It therefore follows that continued efforts to improve the exchanger characteristics listed above play an important part in the activities of resin manufacturing companies.

INORGANIC MATERIALS

References to ion exchange phenomena have been attributed to Old Testament scribes, and later to Aristotle, but the first descriptions in modern scientific terminology have been credited to two English soil chemists, H. S. Thompson and J. T. Way in the mid-nineteenth century. They observed 'base' or cation exchange between calcium and ammonium ions on some types of soil. Upon treating a column of soil with a solution of ammonium sulfate it was found that most of the ammonia was absorbed, whilst the calcium contained originally in the soil was released and passed out of the column. Further studies furnished many sound conclusions as to the nature of ion exchange reactions, some of the more important ones being:

1. Exchange involved equivalent quantities of ions.
2. Certain ions were more easily exchanged than others.
3. The temperature coefficient for the rate of exchange was small.
4. The aluminosilicate fractions of soils were responsible in the main for the exchange although these components rarely took part in the exchange itself.*
5. Materials possessing exchange properties could be synthesized from soluble silicates and aluminium sulfate.

The equivalence law governing the phenomenon was established in the early scientific history of the subject, as also was the fact that some ions were more easily exchanged than others; in other words ion exchangers showed greater selectivity or affinity for different ions. That an exchanger could be chemically synthesized proved to be of the utmost importance; it is for this reason that ion exchange studies and applications have reached such an advanced state today.

The ion exchange capacity of an exchanger is a measure of its total content of exchangeable ions, and is conventionally expressed in terms of the total number of equivalents of ion per kilogram (milli-equivalents per gram) of the exchanger in its dry state and in a given univalent ionic form. As will become evident when describing practical applications, the operating exchange capacity of an exchanger is invariably less than its total capacity. Also because of the presence of 'colloidal humus' in natural soils, exchange capacity data was difficult to systematize and to reproduce in relation to the inorganic minerals which were present. Consequently further studies were carried out utilizing the separated microcrystalline aluminosilicates, or 'clay fractions' of the soil which were obtainable in quite a pure form. These experiments proved that the main exchange agents were indeed contained in the finest or clay-like fractions of soils. Our knowledge of the structure and classification of such materials has shown that some of the inherently finely divided clay materials are directly responsible for the exchange characteristics observed; however, the phenomenon is not purely a property of particle size.

Why the clay minerals should possess an appreciable exchange capacity became more fully understood with the establishment of the crystal structures of the various types, for which most of the early credit is due to W. L. Bragg, L. Pauling, and others. Therefore before

---

* In all soils there is present a fraction called 'colloidal humus' which also contributes to the exchange capacity. This comprises very large, high molecular mass compounds containing organic amino, hydroxy, and carboxylic acid groups originating from vegetable decay, which are often bound with silica and heavy metals such as iron.

the ion exchange relationships of such materials can be fully understood a general appreciation of their structures is essential.

Geologically and genetically, clay minerals are difficult to define simply and adequately, but broadly they are layer lattice silicates of secondary origin. In the same classification are the micas, talc, chlorites, and serpentines which are not strictly clay minerals. In this context, secondary origin means that mineral formation has arisen from the weathering of primary or igneous rock, *e.g.* granites and basalts.

The basic structural unit making up the layer lattice silicates is the silica tetrahedron, $(SiO_4)^{4-}$. When three oxygen atoms of every tetrahedron are linked to similar units a continuous sheet structure is formed which is capable of indefinite extension in two directions at right angles; as a consequence the important physical property of minerals within this group is their plate-like character. One oxygen atom of each tetrahedral unit is not satisfied electrically and requires to be linked to external cations in order to establish electrical neutrality within the lattice. In most structures of this type the silica units are arranged in the form of hexagonal rings, each of which is surrounded by six similar ones, so that bonding takes place by the silica tetrahedra sharing three corners, as shown in Figure 1.1.

Each silica unit in the hexagonal sheet is linked to others through an oxygen atom. The Si—O—Si bond angle can vary, thus giving rise to different conformations of the ring structure, but the majority are based on a bond angle of about 141° 34′. As a result, the single oxygen atoms of each silica tetrahedron which are unsatisfied electrically are oriented in the same spatial direction.

Electrical neutrality in layer lattice silicates is maintained by condensing a sheet hydroxide structure with the sheet of silica tetrahedra (see Figure 1.2). The two types of structure which can take part in combinations of this nature are the hydroxides of divalent elements such as magnesium and those of trivalent elements such as aluminium. In both cases the cations are in six-fold co-ordination with anionic units, but whereas these are entirely hydroxide ions in the case of the pure hydroxide forms (namely brucite and gibbsite respectively) in the layer lattice silicates both hydroxide and oxygen ions are involved. The resulting layer lattice is theoretically electrically balanced within itself, and although the structure is capable of indefinite extension in two dimensions by ionic/covalent bonds, no similar continuity is possible in the direction at right angles to the basal plane. A further condensation of a silica layer in an inverted form above the hydroxide layer can also occur, thus increasing the

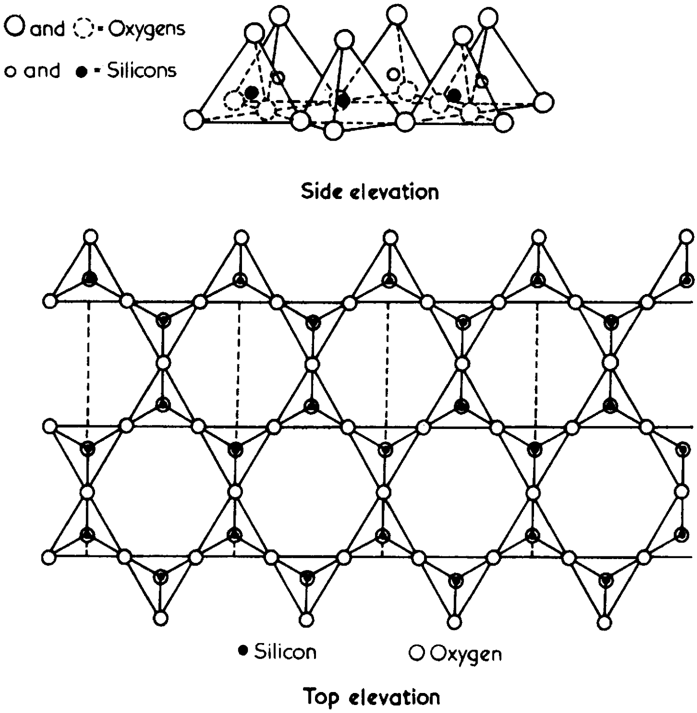


Figure 1.1 *Structure of the ideal silica layer of layer lattice silicates*
(Reproduced by permission from R. W. Grimshaw, 'The Chemistry and Physics of Clays', E. Benn, London, 1971)

size and complexity of the layer and giving rise to other forms of layer lattice silicate minerals.

There are two major subdivisions of layer lattice silicates: a *single layer* type based on a condensation of a hydroxide layer structure with one silica plane and a *double layer* unit in which a further inverted silica plane completes a sandwich-like structure above the hydroxide unit. Each layer lattice is theoretically complete within itself and although similar layers can stack above each other there can be no formal inter-layer ionic or covalent bond formation.

Single Layer Lattice Silicates

Trivalent cations. By far the most common mineral group of this category is that of the kaolin minerals or Kandite group. The cations involved are solely aluminium which are each linked to three hydroxyl units in one layer and to two oxygens and one hydroxyl in the other.

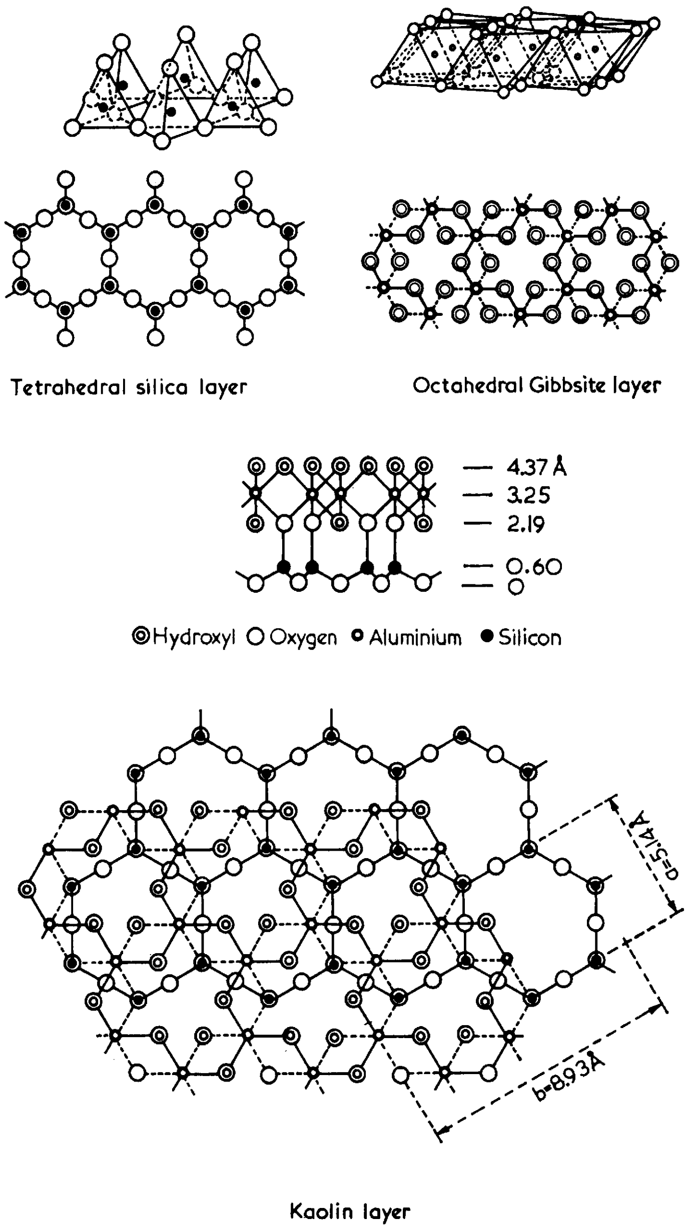


Figure 1.2 *Condensation of silica and gibbsite layers to give the kaolin layer structure* ($\text{nm} = \text{Å} \times 10^{-1}$)

(Reproduced by permission from R. W. Grimshaw, 'The Chemistry and Physics of Clays', E. Benn, London, 1971)

The structure is illustrated in Figure 1.3. The kaolin layer is electrically neutral but extension in the *c*-crystallagraphic direction is possible through hydrogen bonding. This weak linkage results in a plate-like or flaky crystal habit.

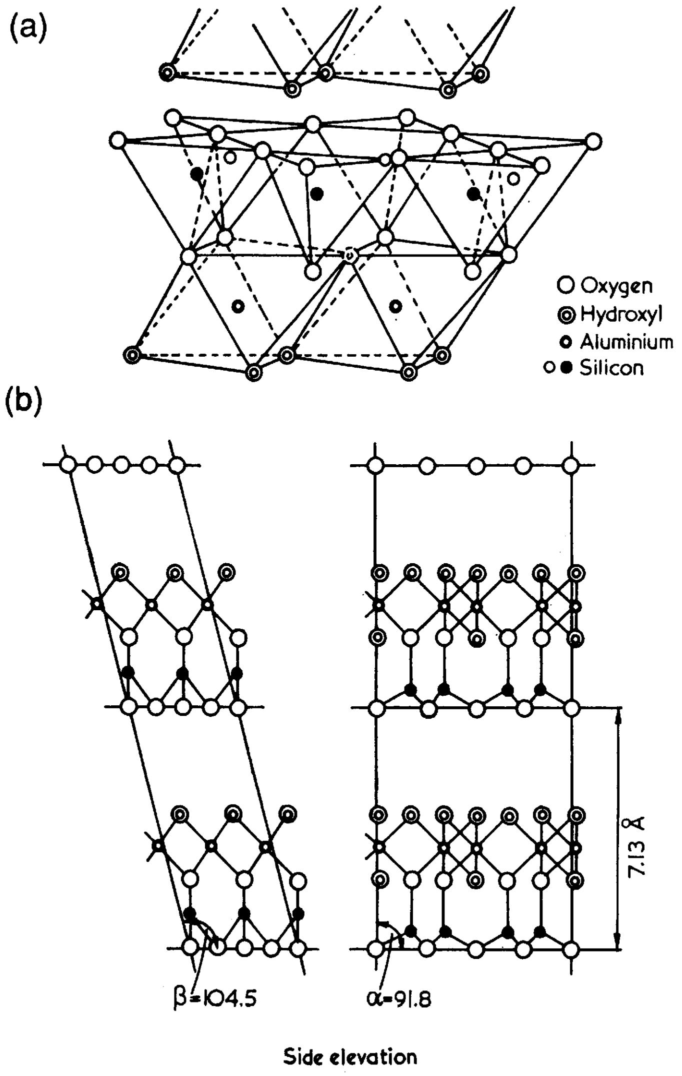


Figure 1.3 *Diagrammatic structures of the kaolin layer*
(Reproduced by permission from (a) R. E. Grim, 'Clay Mineralogy', McGraw-Hill, London, 1953, and (b) R. W. Grimshaw, 'The Chemistry and Physics of Clays', E. Benn, London, 1971)

Because several spatial stacking arrangements are possible there are several kaolin minerals, each with the same chemical composition, namely $Al_2Si_2O_5(OH)_4$, but with different properties. Nacrite, dickite, kaolinite, halloysite, and livesite are well recognized species. No positive evidence has so far been published linking other trivalent cations with a single layer lattice structure, but it has been suggested that iron(III) can replace aluminium in part in the kaolin lattice.

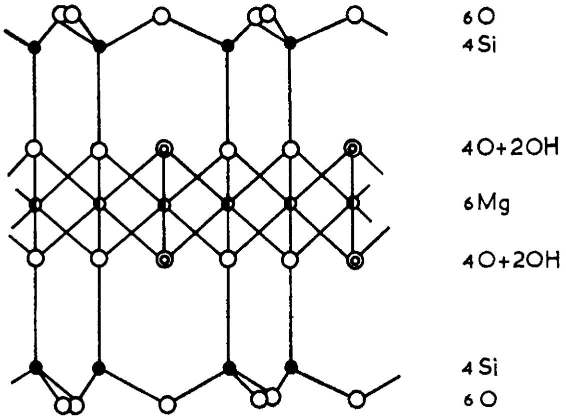
Divalent Cations. Both magnesium and iron(II) can take part in single layer lattice silicate structures although the former is more common. The cations are also in octahedral co-ordination but in order to preserve electrical balance within the lattice, all three of the octahedral sites over each silica hexagonal ring are occupied, as against two in the equivalent kaolin lattice. Divalent cations thus form a *trioctahedral* series whereas the trivalent cation minerals are termed a *dioctahedral* series. The typical magnesium structure is antigorite $Mg_3Si_2O_5(OH)_4$, but there are other minerals of this group which probably differ by virtue of the layer stacking isomerism and in the degree of substitution of ion(II). Chrysotile, the common asbestos mineral, chamosites, and some chlorites are typical examples.

Double Layer Lattice Silicates

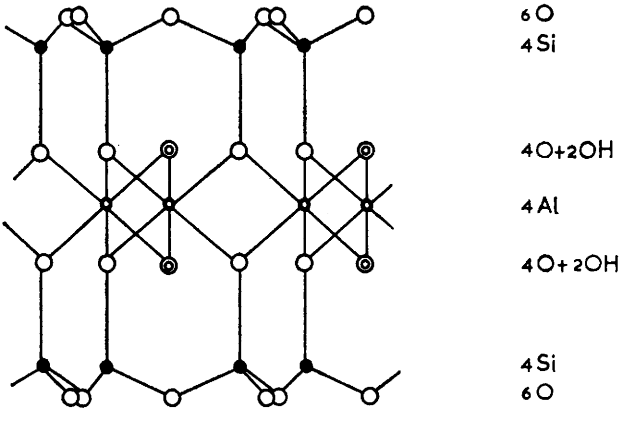
As in the single layer group, two characteristic types of unit are to be found in the double layer silicate minerals based on the valency of the counterbalancing cations. A dioctahedral series, based on pyrophyllite $Al_2(Si_2O_5)_2(OH)_2$ and a trioctahedral group with talc $Mg_3(Si_2O_5)_2(OH)_2$ as the type minerals are well established. These structures are depicted in Figure 1.4. In marked contrast with minerals of the previous group, extensive elemental substitution within the double layer lattice is the rule rather than the exception. Not only does replacement of ions of identical charge and similar size occur but more complex substitution giving rise to charge deficiencies is quite common.

In *micas*, for example, aluminium ions replace silicon in the outermost tetrahedral layers of the lattice thus giving rise to a unit charge deficiency for every replacement. Electrical neutrality is then achieved by incorporating alkali or alkaline earth cations between the individual structural layers. Some typical structural formulae are:

$KAl_2(AlSi_3)O_{10}(OH)_2$ – dioctahedral muscovite mica
$K(Mg, Fe)_3(AlSi_3)O_{10}(OH)_2$ – trioctahedral biotite mica



Talc



Pyrophyllite

Figure 1.4 *Side elevation structures of talc and pyrophyllite*
(Reproduced by permission from R. W. Grimshaw, 'The Chemistry and Physics of Clays', E. Benn, London, 1971)

Montmorillonite minerals or smectites are based on a layer lattice in which the ionic replacement is mainly in the central octahedral layer. Once again the ionic substitution introduces a charge deficiency, typically Mg^{2+} for Al^{3+}. Counterbalancing hydrated cations occupy inter-layer positions, but because the charge deficiencies are situated in the centre of the layer, and are generally smaller in amount, the binding forces are less rigid than those in micas. The extra ions are thus less firmly held and are readily exchanged. Many montmorillonite minerals are known of both dioctahedral and trioctahedral types. Typical montmorillonite and mica structures are shown in Figures 1.5 and 1.6. Other minerals with a double layer structure are chlorites and vermiculites, where lattice charge deficiencies are counterbalanced by either hydroxide layers or hydrated cations between the layers.

All the clay minerals are of relatively small crystallite size, possessing a high specific surface area with many broken edge and surface bonds. In addition, the double layer group minerals frequently contain unbalanced electrical forces within the lattice, all of which have an influence on the overall electrical field surrounding the particles when they are suspended in a polar liquid medium. It is just such complex surface charge properties that play an important role in determining our understanding of such processes as the clarification and filtration of natural water supplies using coagulants such as aluminium sulfate.

ION EXCHANGE PROPERTIES OF THE ALUMINOSILICATES

Single Layer Lattice Silicates

The ideal constitution of the kaolin layer represents an electrically neutral unit, with rarely any isomorphous substitution of cations of different charges within the lattice. Consequently, kaolinite and related minerals would not be expected to show a large cation exchange capacity, and indeed this is usually the case. That a small but varying exchange capacity does occur may be attributed to two principal causes.

1. *Broken Bonds.* The naturally occurring single layer lattice clay minerals do not constitute a perfectly crystalline state, and around the edges of the silica–alumina layers, broken bonds give rise to unsatisfied negative charges which may be balanced by adsorbed cations. The size of the clay mineral particles and the number of lattice distortions play a part in determining the extent of ion exchange capacity, but it remains a matter of some

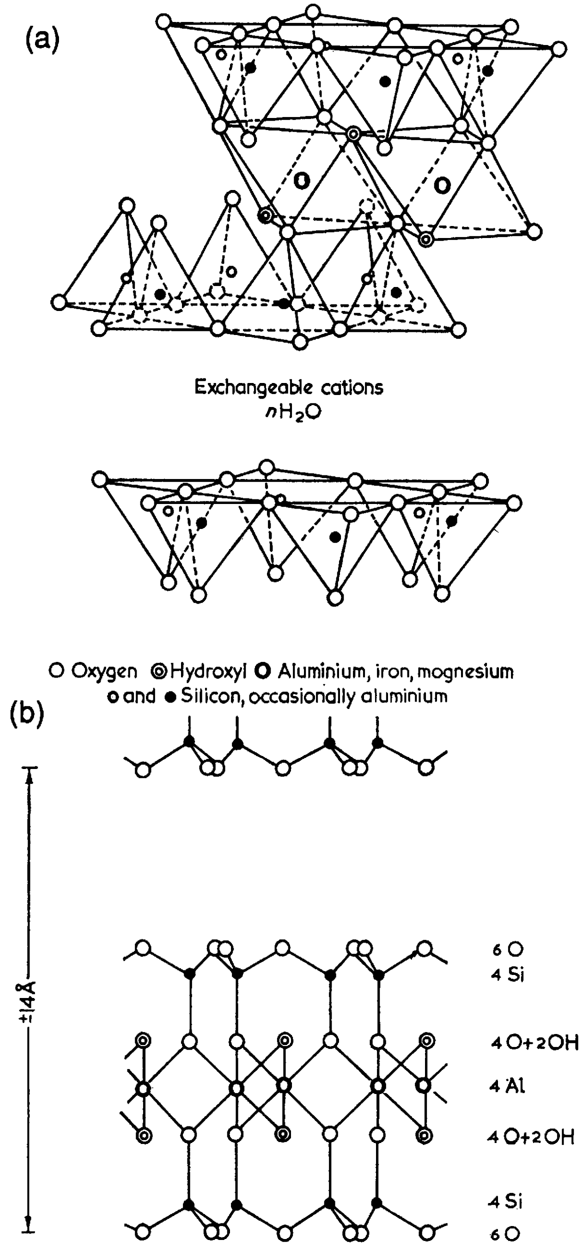


Figure 1.5 *Diagrammatic structure of montmorillonite*
(Reproduced by permission from (a) R. E. Grim, 'Clay Mineralogy', McGraw-Hill, London, 1953, and (b) R. W. Grimshaw, 'The Chemistry and Physics of Clays', E. Benn, London, 1971)

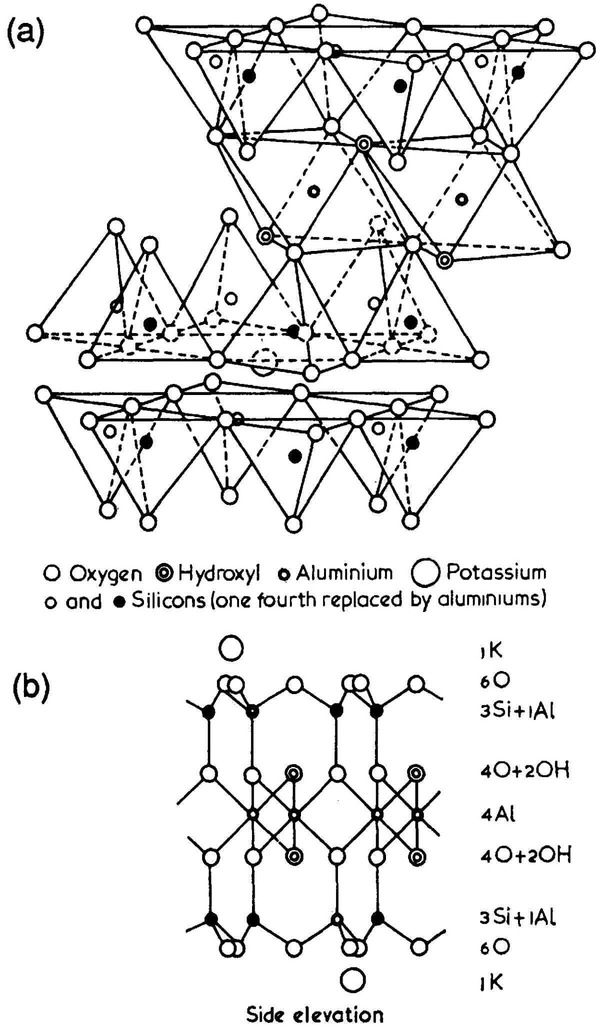


Figure 1.6 *Diagrammatic structure of muscovite mica*
(Reproduced by permission from (a) R. E. Grim, 'Clay Mineralogy', McGraw-Hill, London, 1953, and (b) R. W. Grimshaw, 'The Chemistry and Physics of Clays', E. Benn, London, 1971)

conjecture whether true cation exchange is manifested by extensive breakdown of the crystal lattice (Tables 1.1 and 1.2).

2. *The hydrogen of exposed hydroxyls.* A further contribution to the exchange capacity of clay minerals is made by the hydrogens of

Table 1.1 *Variations in the cation exchange capacity of kaolinite with particle size* (from C. G. Harmon and F. Fraulini, *J. Am. Ceram. Soc.*, 1940, **23**, 252)

Particle size (μm)	*Exchange capacity* (eq kg^{-1})
10–20	0.024
5–10	0.026
2–4	0.036
0.5–1	0.038
0.25–0.5	0.039
0.1–0.25	0.054
0.05–0.1	0.095

Table 1.2 *Cation exchange capacity of kaolinite in relation to the time of grinding* (from W. P. Kelly and H. Jenny, *Soil Sci.*, 1936, **41**, 367)

Mineral	*Exchange Capacity* (eq kg^{-1})
Kaolinite (152 μm)	0.08
Kaolinite ground 48 hours	0.58
Kaolinite ground 72 hours	0.70
Kaolinite ground 7 days	1.01

exposed hydroxyl groups which may be replaced by exchangeable cations. This cause of exchange capacity is of particular significance for clay minerals where there exists an exposed sheet of hydroxyls on one side of the basal cleavage plane. Exposed hydroxyl groups may also exhibit a slight but reversible affinity for exchangeable anions. Isomorphous substitution in the kaolin lattice may occur, but it is not a major contributory factor to the ion exchange capacity unlike the case with some double layer lattice silicates.

Double Layer Lattice Silicates

Some of these minerals possess high cation exchange capacities greatly in excess of that attributable to surface area, crystal fracture and edge effects. The reason for this difference in behaviour arises out of a third and major cause of exchange capacity, namely isomorphous