Sorption and Molecular Sieve Properties of Clays and their Importance as Catalysts [and Discussion]

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Sorption and molecular sieve properties of clays and their importance as catalysts

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Kandites, smectites and vermiculites all form interlamellar inclusion complexes. A comparison has been made between sorption in zeolites, clay minerals and clathrates. In smectites and vermiculites sorption isotherms reflect in contour and behaviour three situations. Kandites show only the first of these, in which the water-free crystals are used and the interlamellar cations, if any, are small inorganic ions (for example Na^+, Ca^{2+}). The guest molecules are polar and penetration of the host occurs with swelling after a threshold pressure or activity is reached. The isotherms may show one or more steps and hysteresis between sorption and desorption cycles is normal. In the second situation all the interlamellar space is filled by long chain organic cations. If a potential guest is imbibed there is further expansion of the host and isotherms sometimes resemble in contour those obtained when benzene is imbibed by rubber. Cohesive energy densities of the interlamellar regions relative to those of the potential guest species strongly influence the interlamellar uptake and the selectivity. In the third situation the clay lamellae are propped apart permanently by cations that do not fill all interlamellar space and are chosen to give vertical free distances between sheets and horizontal free distances between adjacent cations which are of molecular dimensions. The resultant porous crystals behave like zeolite molecular sieves both in the contours of isotherms for the interlamellar part of the sorption and in the molecule sieving effects that have been obtained.

In addition suitably modified or natural clay minerals can catalyse many kinds of reaction. These include cracking, isomerization, dimerization, and oligomerization, redox reactions and hydrogen transfer, hydration and dehydration, esterification, lactonization, etherification, conversion of primary to secondary amines and reaction between guest and interlamellar organic cations. Some comments on and examples of certain of these processes are given.

1. Introduction

Interlamellar inclusion of guest species is a notable characteristic of 1:1 and 2:1 sheet silicates (kandites, smectites and vermiculites). Inclusion is facilitated because the forces binding the sheets to one another are not chemical but physical, that is, dispersion, close range repulsion, hydrogen bonding, and especially for smectites, vermiculites and micas, electrostatic (Jenkins & Hartman 1982) interactions. For kandites the ideal composition is $Al_2Si_2O_5(OH)_4$. For the 2:1 sheet silicates the negative charge on the lamellae varies between zero for an ideal pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, to a maximum of about 500 meq 100 g^{-1} for margarite micas. The charge densities of a number of 2:1 sheet silicates have been tabulated by Weiss (1958*a*) as the area per unit charge. Some of these values are given in table 1. Swelling in water can, in the Na-clay minerals of charge density corresponding with areas of 47 to at least 100 Å^2† per unit charge, result in complete dispersion of smectite lamellae. Swelling is zero for the most highly charged mica lamellae (margarite) and also for uncharged lamellae of pyrophyllite and talc.

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† 1 Å = 0.1 nm = 10^{-10} m.

Table 1 also shows that for a given lamellar charge density the charge on the interlamellar cation can modify the swelling behaviour. Thus the Ca-forms of the clay minerals swell in water to a different extent to the Na-forms at the same charge density. When crystals that swell in water are exposed to water vapour at various relative humidities (r.h.) and the $d(001)$ spacings at equilibrium are plotted against r.h. there tend to be plateaux at uptakes which have been interpreted as representing completion of one- or two-layer hydrates between each pair of lamellae (figure 1) (Gillery 1959). In the same connection the isotherms tend to show steps, as illustrated for water in Mg-vermiculite (figure 2) (van Olphen 1969). As with the 2:1 sheet silicate pyrophyllite, water does not intercalate between the 1:1 sheets in kandites, the lamellae of which ideally carry no negative charge so that there would be no interlamellar cations. Halloysite, $Al_2(Si_2O_5)(OH)_4 \cdot 2H_2O$, in which there is a single layer of water molecules between each pair of lamellae, is an exception. However, when this water is removed by heat and evacuation the process is irreversible: no water can subsequently be intercalated.

Table 1. Charge density and swelling of clay minerals in distilled water (Weiss 1958*a*)

mineral	area per unit charge Å²	swelling for interlamellar cations Å Na⁺	Ca²⁺
margarite	12	0	0
muscovite	24	1.9	2.8
biotite	24	1.9	2.8
lepidolite	24	1.9	2.8
seladonite	27	2.4	2.8
glauconite	31	3.8	2.8
trioctahedral illite	36	5.1	4.3
vermiculite	37	5.1	4.3
beidellite I	41	5.4	4.9
nontronite	46	∞	9.2
beidellite II	57	∞	9.2
montmorillonite I	60	∞	9.2
montmorillonite II	75	∞	9.6
hectorite	100	∞	10.6
pyrophyllite	∞	0	0
talc	∞	0	0

2. Inclusion by zeolites, clay minerals and clathrates: a comparison

Inclusion by zeolites, clay minerals and clathrates can be of technical importance, and a comparison of some typical features is of particular interest (table 2). In table 2 under the heading of clay minerals, A and B denote different types of sorbent. Thus type A sorbents can intercalate guest molecules only when they expand as uptake proceeds. Type B sorbents on the other hand have been expanded and made permanently porous by exchange using cations of chosen shapes and sizes as props or pillars (§ 4).

Isotherms for interlamellar sorption in clay mineral sorbents of type A often show steps, as in figure 2, and as often happens in clathrates (Allison & Barrer 1968). On the other hand isotherms in type B sorbents are continuous (§ 4). Interlamellar sorption can be regarded as a type of solution, just as for sorption in zeolites or clathration. At an equilibrium pressure, p, of

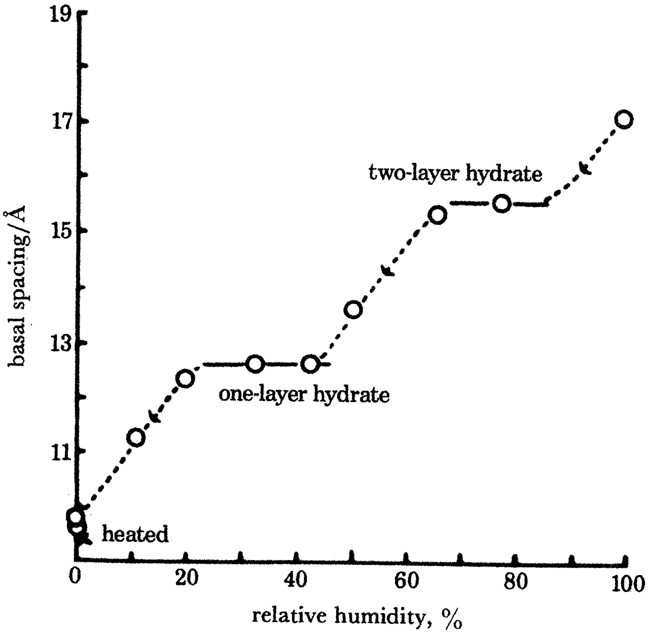


FIGURE 1. Relation between *d*(001) and percentage relative humidity for water in a natural Na-montmorillonite (Gillery 1959).

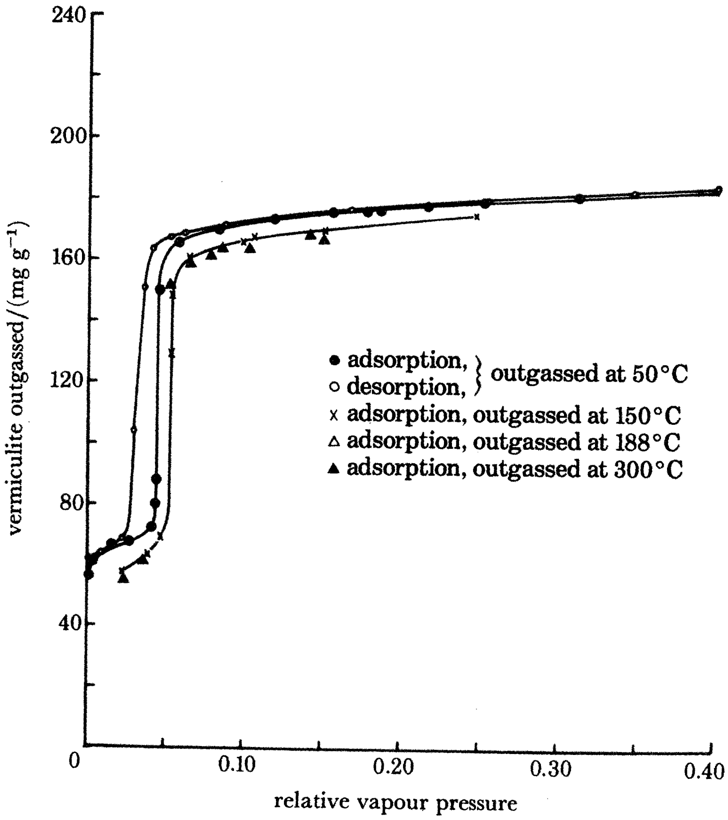


FIGURE 2. The stepwise sorption isotherm of water at 50 °C in vermiculite outgassed at various temperatures (van Olphen 1969).

the guest the lowering in chemical potential of the host crystal, $\Delta\mu$, owing to uptake of the guest is (Barrer 1960)

$$\Delta\mu = (\mu-\mu^0) = \int_0^p \frac{V\,dp}{(1-X_G)} - RT\int_0^p \frac{X_G\,dp}{(1-X_G)p} \tag{1}$$

where μ and μ^0 are chemical potentials of the lattice-forming units of the host crystal containing the guest molecules and when empty respectively; X_G is the mole fraction of the guest species in the host–guest solution; and V is the volume of one mixed mole of the solution. The gaseous phase of the guest is assumed ideal. For pressures normally involved the first integral is small. The second integral can be evaluated by graphical integration once the isotherm is known.

TABLE 2. COMPARISON OF ASPECTS OF INCLUSION OF GUEST MOLECULES IN ZEOLITES, CLAY MINERALS AND CLATHRATES

zeolites	clay mineral sorbents	clathrates
porosity permanent and stable; pores and channels of molecular dimensions	(A) porosity absent until $d(001)$ expanded by guest (B) permanent porosity created before sorption	porosity created by recrystallization of host in presence of an adequate vapour pressure of guest
isotherms normally continuous and of Type I†	(A) isotherms often stepped (B) isotherms continuous and of Type I†	isotherms continuous and of Type I† over region of vapour pressure of guest in which clathration occurs; no uptake below this region
guest molecules distributed spatially according to numerous channel and cavity patterns ↘	guest molecules in layers ↓	guest molecules normally isolated in cavities or channels ↙
	guest molecules oriented in some examples; 'lock and key' relations between guest and host sometimes shown	
guest removable with minimal unit cell change	(A) guest removable with decrease in $d(001)$ (B) guest removable with minimal change in $d(001)$	guest removal causes recrystallization of host to the compact non-porous original form
external area small compared with intracrystalline area	external surface can be more important than for zeolites	external area small; uptake inside crystals only
ion exchange can modify sorption often profoundly	ion exchange can modify sorption, often profoundly (but kandites and pyrophyllite have no inter-layer exchange capacity)	ion exchange properties are absent

† In the Brunauer classification (Brunauer 1944).

Equation (1) refers to host crystals already opened to accept the guest molecules without perceptible changes in lattice structure (as for zeolites and the permanently porous clay mineral sorbents of type B). In clathration, or when the clay minerals have first to expand to accommodate the guest molecules (sorbents of type A) one must add to $\Delta\mu$ an extra free energy term $\Delta\mu_{\alpha\beta}$ which represents the increase in chemical potential when the denser or α-phase of the host is changed to the empty porous or β-phase, free of the guest species. For inclusion of guest molecules at the pressure p the sum

$$\Delta\mu + \Delta\mu_{\alpha\beta}$$

must be negative. This means that p must be such that

$$-RT\int_0^p \frac{X_G\,dp}{(1-X_G)p} \quad \text{exceeds} \quad \Delta\mu_{\alpha\beta}+\int_0^p \frac{V\,dp}{(1-X_G)}.$$

There can therefore sometimes be a measurable threshold pressure below which clathration or inclusion in clay mineral sorbents of type A does not occur. This behaviour is shown for pyridine and water in Na-montmorillonite in figure 3 (Barrer & McLeod 1954). The isotherms represent the sum of adsorption on external surfaces plus inclusion between the clay lamellae. Because of this and because of imperfections in the small host crystals the steps are not sharp. The water isotherm indicates more than one stage and reflects the stages in expansion seen in figure 1. That is, after completion of an interlamellar monolayer of water, there is a further expansion to accommodate a second layer, followed by still further expansion to accommodate still thicker layers. Quantitative modelling of this behaviour provides an interesting challenge.

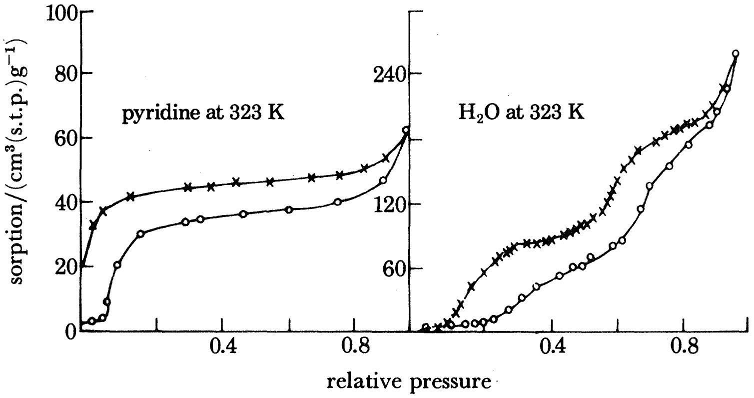


FIGURE 3. Sorption of pyridine (left) and water (right) in natural Na-rich montmorillonite, showing threshold pressure, isotherm steps and hysteresis (Barrer & McLeod 1954).

The onset of inclusion at a critical pressure sometimes observed for type A sorbents is further modified because the expanded host lattice has to nucleate from the parent phase at the edges of the clay lamellae. This introduces two new free energy terms: Δg_σ due to interfacial free energy; and Δg_s due to misfit and hence strain between the nucleus and the parent lattice. Δg_σ and Δg_s are both positive and so tend to delay the onset of interlamellar penetration beyond the true equilibrium threshold pressure. Conversely on desorption a Δg_σ and Δg_s again arise, this time delaying the nucleation of the collapsed guest-free phase of the host lattice when the vapour pressure of the guest falls below the equilibrium threshold value. As a result hysteresis can occur between sorption and desorption cycles (figure 3).

3. Clay mineral sorbents of type A

As already noted, type A sorbents cannot include guest molecules without expansion of the $d(001)$ spacing. There are however two subdivisions of these sorbents which behave very differently.

Type A1. This group comprises smectites and vermiculites having exchangeable inorganic cations such as Li^+, Na^+, K^+, Mg^{2+} or Ca^{2+} between the lamellae; and kandites which ideally are free of interlamellar cations.

Type A2. These sorbents comprise organo-clay minerals in which, by ion-exchange, the inorganic cations are replaced by alkylammonium ions with long chain alkyl groups sufficiently large to fill all the available interlamellar space. Even organo-mica of this type can be made by exchange of K^+, although the process occurs with extreme slowness (Weiss 1958*b*). In this organo-mica the area available per chain is about 24 Å² (table 1), which is about the cross-sectional area of a chain normal to the basal surfaces. As the charge density decreases (vermiculites and smectites) the area available per chain increases (table 1), chain orientation can be less steep (vermiculites) while in smectites the chains may often lie parallel with the basal surfaces, as evidenced by the $d(001)$ spacings. For all sorbents of type A2 however the chains must fill the interlamellar region.

TABLE 3. SOME ONE- AND TWO-LAYER COMPLEXES OF ORGANIC MOLECULES IN Ca-MONTMORILLONITE (BRINDLEY & RAY 1958)

guest	$d(001)$/Å one layer	$d(001)$/Å two layer	one layer spacing − 9.5 Å	probable orientation of chain zigzag to basal surfaces
acetylacetone	13.0_0	17.1	3.5_0	$\parallel$
α-methoxyacetylacetone	13.0_0	16.9_5	3.5_0	$\parallel$
acetoaceticethylester	13.1_0	17.1_5	3.6_0	$\parallel$
nonanetrione-2,5,8	13.1_0	17.3_5	3.6_0	$\parallel$
hexanedione-2,5	13.0_5	16.8_5	3.5_5	$\parallel$
β, β′-oxydipropionitrile	13.1_5	15.7_5	3.6_5	$\parallel$
β-ethoxypropionitrile	13.2_5	—	3.7_5	$\parallel$ (?)
bis-(2-ethoxyethyl)-ether	13.4_0	16.7_5	3.9_0	$\perp$
bis-(2-methoxyethyl)-ether	13.2_5	17.0_0	3.7_5	$\perp$
ethyleneglycoldiglycidether	13.4_0	17.6_0	3.9_0	$\perp$
triethyleneglycol	13.3_0	17.3_5	3.8_0	$\perp$
diethyleneglycol	13.3_0	15.7_5	3.8_0	$\perp$
triethyleneglycoldiacetate	13.3_5	16.5_0	3.8_5	$\perp$
diethyleneglycoldiacetate	13.1_5	16.5_5	3.6_5	$\parallel$ (?)
hexanediol-1,6	13.5_5	17.4_5	4.0_5	$\perp$
pentanediol-1,5	13.6_5	17.4_5	4.1_5	$\perp$
2,3-hexadiynediol-1,6	13.0_5	16.1_0	3.5_5	$\parallel$

3.1. *Inclusion by sorbents of type A1*

Intercalation by well outgassed smectites and vermiculites of type A1 normally requires that the guest molecules should be polar, because of the high polarity of the sorbents. Some characteristics of this group of sorbents are already outlined in § 1 and 2. The $d(001)$ spacings for some organic guest species in Ca-montmorillonite (Brindley & Ray 1958) serve to illustrate other inclusion complexes (table 3). The spacings have been interpreted as owing to one or two monolayers of the organic molecules between the clay lamellae. The molecules all lie along the basal surfaces, but the zigzag of the chain can lie flat on the basal surfaces (giving monolayer thicknesses *ca.* 3.5_0 to 3.6_5 Å) or perpendicular to these surfaces (monolayer thicknesses *ca.* 3.7_5 to 4.1_5 Å).

Glycol- and glycerol-smectite complexes have double layers with $d(001)$ *ca.* 17.4 Å and *ca.* 17.7 Å respectively. Each also intercalates in vermiculites as layers one and sometimes two molecules thick. Nitriles, amines, diamines, glycine and its peptides and even proteins and other polymers are among the species which can be intercalated in sorbents of type A1.

Kaolinite forms intercalation complexes (Barrer 1978) involving the very polar or ionic species urea, formamide, hydrazine, acetamide and salts of organic acids (Li-, Na-, K-, Rb-Cs-, NH_4- and N_2H_5- acetates; K-, Rb- and Cs-propionates; and K-cyanoacetate). The guest often forms a monolayer *ca.* 2.9–3.8 Å thick. However, K-, Rb-, Cs- and NH_4-acetates and K-cyanoacetate give thicker layers from *ca.* 5.8–10 Å. Kaolin demonstrates other features of interest. Thus, as shown in figure 4 (Weiss *et al.* 1963) the kinetics of uptake of formamide have the sigmoid form expected for penetration only after nucleation of the expanded phase (§ 2).

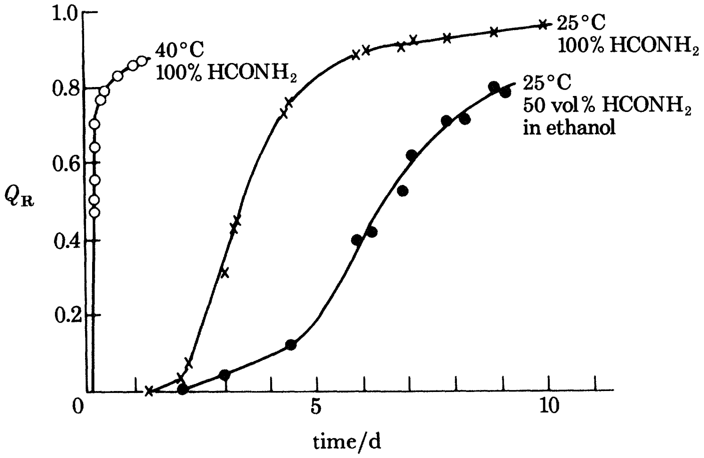


FIGURE 4. Degree of intercalation, Q_R, as a function of time and temperature for formamide in kaolinite. The figure illustrates the induction period for the nucleation of the expanded phase (Weiss 1963).

TABLE 4. *d*(001) VALUES FOR COMPLEX FORMED WITH THE ASSISTANCE OF 24% HYDRAZINE IN WATER (WEISS *ET AL.* 1963)

potential guest	*d*(001)/Å in aqueous hydrazine solution of guest	after hydrazine solution replaced by aqueous solution of guest
K-acetate	10.4	14.0
Na-acetate	10.4	10.0_6
K-oxalate	10.4	10.2_8
K-glycollate	10.7	12.4_4
K-alaninate	10.7	12.4_5
K-lysinate	10.6	14.8_8
K-lactate	10.6	11.1_8
glycerine	10.4	10.5_2
n-octylamine	31.7_1	31.7_1
benzidine†	10.6	10.8

† Benzidine in 24% hydrazine in aqueous alcohol.

The uptake is also pH and temperature sensitive. NH_4-acetate for example was intercalated only in the pH range 7–10.5. Between 0 and 25 °C the rate of uptake increased rapidly but above 40 °C no intercalation occurred. If the 14.0 Å complex was first prepared at low temperature and was then heated while still in the acetate solution to 65 °C the *c*-repeat distance increased to 17.1_5 Å. The repeat distance in the parent kaolinite is 7.2 Å so that the interlamellar layer of NH_4-acetate has risen from 6.8 Å to 9.9_5 Å in thickness.

The number of compounds that can be intercalated in kaolin can be increased by including in the aqueous phase not only the potential guest but also a second species such as hydrazine which can intercalate directly and independently. Examples are given in table 4 in which complexes first form from solutions of various species in 24% aqueous hydrazine. When the hydrazine component is now removed the aqueous guests swelled the kaolinite as shown in the final column of table 4. The spacing *ca.* 10.7 Å is found for hydrazine acetate solutions in absence of other guests.

3.2. *Organo-clay sorbents of type A2*

As noted in § 3 in these sorbents the interlamellar space is fully occupied by long chain organic cations. For alkyl chains of carbon number up to about 10 the chains can lie along the basal surface but for still longer chains the thickness of the organic layer rises from the monolayer value of *ca.* 3.5 Å to about 7 or 8 Å, which could represent bi-layers of ions possibly with some excess interlamellar alkylammonium salt. In partially ion-exchanged N-montmorillonites there is clear evidence of randomly interstratified layers containing either the organic or the inorganic ion but not both, when the entering ions were $NH_3^+CH_3$ or $N(CH_3)_4^+$ (Barrer & Brummer 1963). This behaviour could be general for partial exchanges with alkylammonium ions.

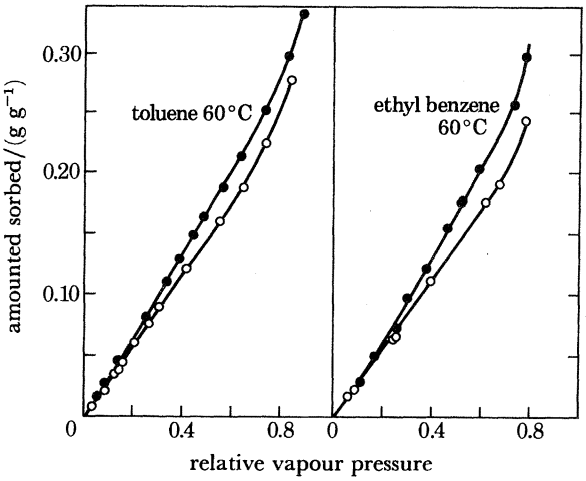


FIGURE 5. Isotherms for toluene and ethyl benzene obtained with Bentone 34 (dimethyldioctadecylammonium montmorillonite) (Barrer & Kelsey 1961 *b*). ○, Adsorption; ●, desorption.

Whatever the packing and orientation of the alkyl chains in fully exchanged organo-clays these chains provide beds of interlamellar material of low cohesive energy density. The organo-clay sorbents of type A2 now imbibe not only polar but also non-polar guest species, by mixing of these species with the alkyl chains of the organic cations. Isotherms for toluene and ethyl benzene in dimethyldioctadecylammonium montmorillonite (Bentone 34) are shown in figure 5 (Barrer & Kelsey 1961 *b*), which represent total sorptions on external surfaces and between the lamellae. Where interlamellar uptake is large, as for toluene and ethylbenzene, the isotherm contours recall those when benzene and other hydrocarbons are imbibed by rubber (Gee 1942), and are greatly changed in shape from those in type A1 sorbents (figures 2 and 3). The isotherm contours support the view that sorption involves mixing of hydrocarbon and alkyl chains. Such mixing involves further swelling of the clay sorbent and also the extent of uptake at a given relative pressure, p/p_0, of the guest is a function of its cohesive energy density (c.e.d.). These features are illustrated in table 5. The uptake at a given relative pressure and temperature should be a maximum for a c.e.d. which matches most nearly that of the interlamellar region as modified by the influence of the adjacent lamellae. The largest uptake was observed with pyridine. The very limited swelling for *n*-heptane and cyclohexane indicates that interlamellar uptake is slight, so that much of the observed total sorption is here on external sufaces of the sorbent. Interlamellar uptake is a very selective function of $\delta = \rho^{\frac{1}{2}}$, where ρ is the c.e.d. and is not closely related to molecular size and shape differences as in the case of molecule sieving by zeolites.

Table 5. Correlation of sorption by Bentone 34 (alcohol extracted) with cohesive energy density (c.e.d., ρ) of guest species (Barrer & Kelsey 1961*a*)

guest	$\delta = \rho^{\frac{1}{2}}$, at 25 °C (cal‡ $cm^{-3})^{\frac{1}{2}}$	T °C	sorption at T and $p/p_0 = 0.2$	sorption at T and $p/p_0 = 0.6$	swelling at T and $p/p_0 = 0.6$
			mmol g^{-1}		A°
iso-butane	6.25	−30	0.06_2	0.21	—
n-butane	6.7	−30	0.07_7	0.22	—
iso-octane	6.85	45	0.11	0.31	—
n-heptane	7.45	45	0.11	0.34	0.4
cyclohexane	8.20	45	0.16	0.48	0.4
ethylbenzene	8.80	60	0.52	1.60	—
toluene	8.90	45	0.65	1.93	11.8
benzene	9.15	45	0.81	2.33	11.2
dioxane	10.0	60	0.92	2.07	—
pyridine	10.7	60	1.79	3.08	—
nitromethane†	12.6	45	1.38	2.54	—

† Purity not known.
‡ Cal = calorie. 1 calorie = 4.187 J.

The selectivity shown by Bentone 34 towards different potential guests has led to its successful use in a variety of chromatographic separations. These include separations of mixtures of ethylbenzene, *p*-xylene, *o*-xylene and *m*-xylene (van Rysselberge & van der Stricht 1962); of aromatic and aliphatic compounds (White 1957); of toluidines and cresols (White 1959); of benzene and its di- and trichloro derivates (Cowen & Hartwell 1961); and of *o*-, *m*- and *p*-isomers of terphenyl, phenoxyphenyl and nitrophenol (Kiselev *et al.* 1972).

4. Sorbents of type B

In sorbents of type B the exchange ions expand the clay mineral but do not fill all the interlamellar space, so that there are pathways among the ions. The ions must be large enough to hold the clay lamellae apart by distances comparable with the dimensions of the guest. Provided lateral free distances between adjacent ions are also of molecular dimensions permanent interlamellar porosity is available, just as with zeolites, for selective uptake of guests on the basis of size and shape differences of the molecules of competing guest species. This behaviour was first envisaged and studied in the 1950s in the author's laboratory (Barrer & McLeod 1954, 1955; Barrer & Hampton 1957; Barrer & Reay 1957). The exchange ions introduced were $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$. This work was developed and extended using the above and other cations until the mid 1970s (Barrer & Perry 1961*a*, *b*; Barrer & Kelsey 1961*a*, *b*; Barrer & Brummer 1963; Barrer & Millington 1967; Barrer & Jones 1971; Craven 1976), and has recently been further extended in several laboratories

(Mortland & Berkheiser 1976; Shabtai *et al.* 1976; Vaughan & Lussier 1980; Ocelli *et al.* 1981; Pinnavaia *et al.* 1983). It has been shown that sensitive molecule sieving is possible with these new kinds of sieve (Craven 1976) in full parallel with zeolites. By changing the size and shape of the entering exchange ions, by selecting or making smectites and vermiculites of differing exchange capacities and by altering the charge of the entering exchange ions one may vary and control both lateral and vertical free distances in the resultant interlamellar cavities and channels. Access to these tailor-made cavities and channels involves diffusion of guests in two dimensions in each interlamellar region.

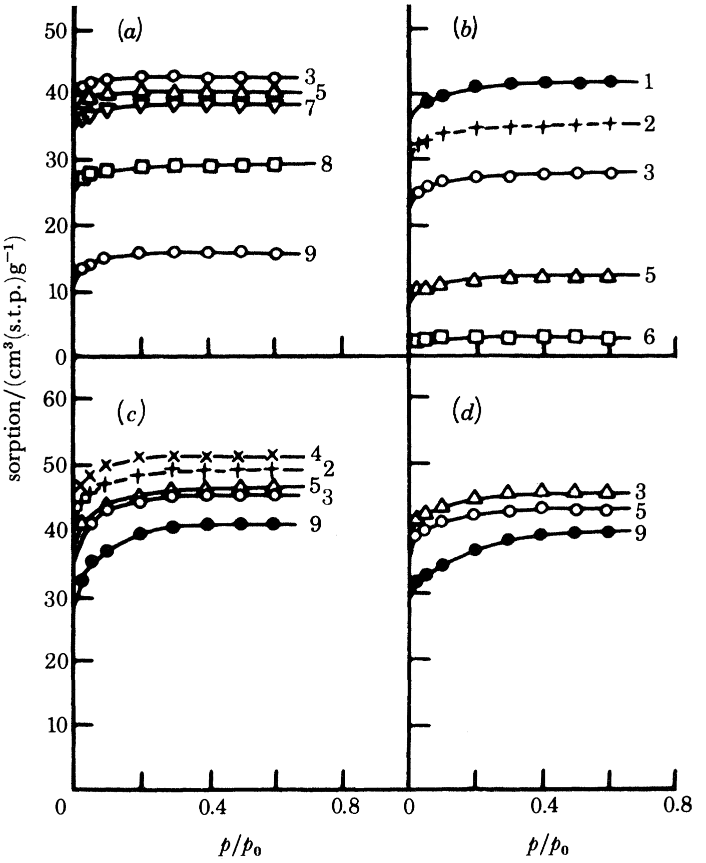


FIGURE 6. Estimated interlamellar sorptions of N_2 and Ar at 78 K (Barrer & Millington 1967). (*a*) N_2 in alkyldiammonium montmorillonites; (*b*) N_2 in alkylammonium montmorillonites; (*c*) N_2 in alkyldiammonium hectorites; and (*d*) Ar in alkyldiammonium hectorites. The numbers by the curves are the carbon numbers of the organic ions.

A sorption isotherm for these expanded, permanently porous clay minerals is a composite of that on external surfaces of the crystals and that between the clay sheets. The total isotherm can therefore be of Type I or Type II in Brunauer's classification. If the isotherm of N_2 at 78 K is measured on the parent non-porous Na-smectite and then on a series of its expanded porous forms in which the exchange ions are, for example, alkyl- or dialkylammonium ions and the isotherm for the non-porous Na-smectite is subtracted from those for the porous forms the difference could be expected to approximate to the interlamellar parts of the sorption. Such difference isotherms obtained with organo-smectites are shown in figure 6 (Barrer & Millington 1967) for N_2 and Ar at 78K. Just as with zeolites they are all of Type I. As the carbon number of the exchange ion increases (indicated by the numbers on the curves) the saturation interlamellar uptake decreases. This is as expected for alkyl chains parallel with basal surfaces of lamellae because more and more interlamellar free volume is occupied by the chains. Eventually, as discussed in § 3.2, permanent intracrystalline porosity becomes negligible and the sorbents become fully of type A2.

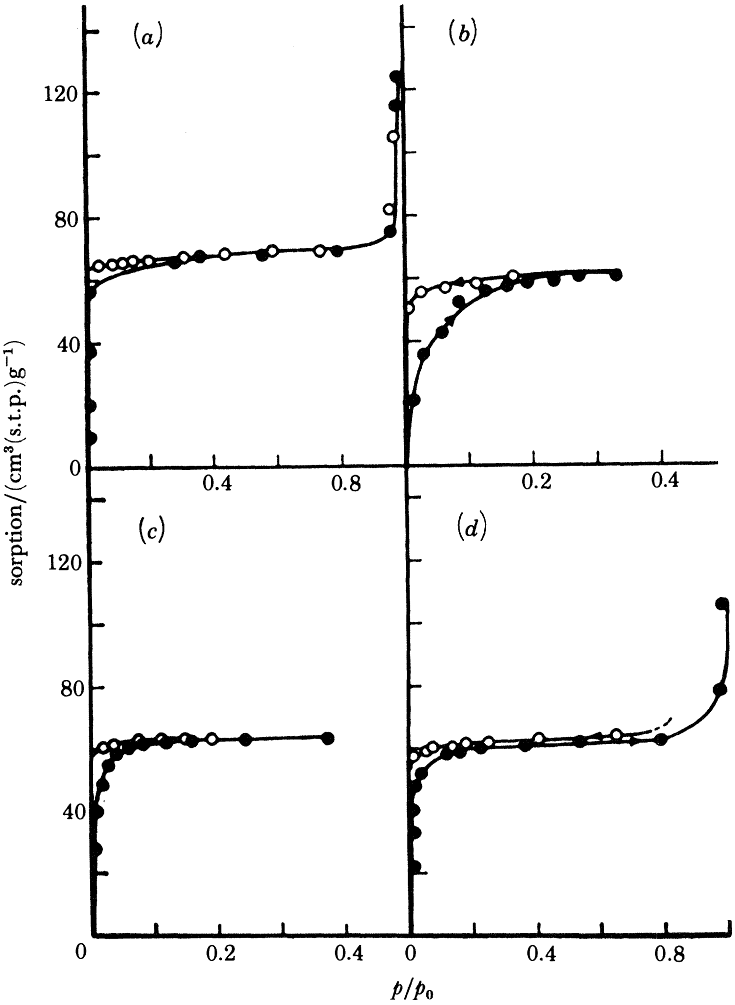


FIGURE 7. Isotherms of O_2, N_2 and Ar in en-FH90 (en = ethylenediammonium) (Barrer & Jones 1971). (*a*) O_2 at 78 K, allowing 20 min per isotherm point; (*b*) N_2 at 78 K, allowing 15 min per point; (*c*) O_2 at 90 K, 20 min per point; and (*d*) Ar at 78 K, 30 min per point.

As an alternative to estimating intracrystalline sorption isotherms of smectite sorbents of type B by the above difference method much larger crystals of fluorhectorites were synthesized by sintering and melt procedures (Barrer & Jones 1971). For these as for zeolites sorption on external surfaces becomes very small. Isotherms of O_2, N_2 and Ar at 78 or 90 K are shown in figure 7 for ethylammonium fluorhectorite of exchange capacity 90 meq 100 g^{-1} (termed en-FH90). Except at the highest relative pressures all are of Type I.

Examples of interlamellar saturation capacities for N_2 at 78 K are given in column 7 of table 6 for some alkylammonium and alkyldiammonium smectites. The calculated interlamellar free areas were obtained as follows. The N_2 isotherms on the Na-montmorillonite or hectorite gave external areas appropriate to average values of 26 and 9 lamellae per crystal. Crystals containing these numbers of lamellae have total interlamellar areas of 270×10^3 and 250×10^3 m^2 per gram unit cell (g.u.c.). From these areas one must subtract areas occupied by cations after allowing for the fractions of the total cations on external areas. These fractions were estimated as 4 % for montmorillonite and 11 % for hectorite. Areas per cation were estimated from their lengths multiplied by 4.6 Å, corresponding with ions lying along basal surfaces (table 6, column 3). The total interlamellar area less that occupied by the interlamellar ions then gives the calculated interlamellar free area of table 6 column 4. The $d(001)$ repeat distance of table 6 column 5 less 9.4 Å was taken as the vertical free distance. The free area multiplied by this distance gives a free volume, not tabulated, and from the free volume and the molar volume of N_2 at 78 K (34.8 $cm^3\ mol^{-1}$) the calculated saturation capacities of column 6 were obtained. The ratio of the observed saturation (column 7) to that calculated is given in column 8.

At 78 K these ratios show an interesting trend. For the alkyldiammonium hectorites observed and calculated sorption capacities are not very dissimilar. However for the alkylammonium montmorillonites the ratios decline strongly from about 1 for $CH_3NH_3^+$ to 0.12 for $C_6H_{13}NH_3^+$. It seems likely that at 78 K chains are immobile along basal surfaces and that juxtaposition of the CH_3 ends of alkyl chains can lead to nearly closed loops of chains from which N_2 is excluded. Such behaviour is not possible for an ion as small as $CH_3NH_3^+$ but is more and more likely as the chains increase in length. The above effect should occur less often with alkyldiammonium smectites, where both ends of the ions are -NH_3^+ and so would repel other ends. Moreover, because these ions carry two charges they are only half as numerous as the alkylammonium ions. For both reasons the ratios of observed to calculated saturation values should decline less rapidly with carbon number for the alkyldiammonium smectites.

The extreme sensitivity of low temperature access to the interlamellar region of some permanently porous clays is shown in figure 8 (Craven 1976) for $Co^{III}(en)_3$-fluorhectorite of exchange capacity 150 meq 100 g^{-1} (Barrer & Jones 1971), designated as $Co^{III}(en)_3$-FH150. Here 'en' denotes ethylene diamine. The van der Waals dimensions of O_2 and N_2 are respectively 2.8×3.9 and 3.0×4.1 Å so that at 78 K these small dimensional differences serve to differentiate O_2 and N_2 in a remarkable way. These differences are reflected in the sorption rates, which were at *ca.* 77 K extremely fast in $Co^{III}(en)_3$-FH150 for H_2, D_2, Ne and O_2 but very slow for N_2, Ar and CH_4 (Craven 1976). One can produce in clay mineral sorbents of type B rate and selectivity differences based on molecular shape and size differences just as remarkable as those found with zeolite molecular sieves.

Selectivites in $N(CH_3)_4$-montmorillonite are illustrated in figure 9 (Barrer & Perry 1961 *b*) for the pairs benzene-*n*-heptane, benzene-cyclohexane and cyclohexane-*n*-heptane. These are equilibrium isotherms. $N(CH_3)_4$-montmorillonite gave excellent chromatographic separations of *n*-heptane from isooctane and from cyclohexane (Barrer & Hampton 1957). Sorption in ethylenediammonium fluorhectorite (en-FH90) suggested that *n*-paraffins and, or, aromatics could be separated from paraffins with a quaternary carbon or from cyclohexane. En-FH150 behaved in a significantly different way. It sorbed benzene but not toluene, *m*-xylene or mesitylene under the conditions employed. Like en-FH90 it sorbed *n*-paraffins but did not intercalate paraffins with a quaternary carbon atom (Barrer & Jones 1971). $Co^{III}(en)_3$- and $Cr^{III}(en)_3$-montmorillonite gave good separations of C_1 to C_5 hydrocarbons on very short

TABLE 6. OBSERVED AND CALCULATED INTERLAMELLAR SATURATION CAPACITIES (CM^3 (AT S.T.P.) G^{-1}) FOR N_2 AT 78 K IN SOME ORGANO-CLAYS (BARRER & MILLINGTON 1967)

cation	gram unit cell mass	area of ion Å^2	calculated free area m^2 g^{-1}	$d(001)$ Å	calculated saturation	observed saturation	observed saturation / calculated saturation
			(*a*) alkylammonium montmorillonites (c.e.c. 85 meq 100 g^{-1})				
$CH_3\overset{+}{N}H_3$	746	21.6	294	11.6	$41._7$	$41._5$	0.99
$C_2H_5\overset{+}{N}H_3$	755	29.8	214	12.8	$46._9$	35	0.74
$C_3H_7\overset{+}{N}H_3$	765	35.6	184	13.1	$43._7$	$27._5$	0.63
$C_5H_{11}\overset{+}{N}H_3$	783	47.1	126	13.4	$32._1$	$12._5$	0.39
$C_6H_{13}\overset{+}{N}H_3$	792	52.9	98	13.4	$25._0$	3	0.12
			(*b*) alkyldiammonium montmorillonites (c.e.c. 85 meq 100 g^{-1})				
$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	750	40.6	262	12.9	$59._1$	43	0.73
$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	759	52.2	231	13.3	$57._8$	40	0.69
$\overset{+}{N}H_3(CH_2)_7\overset{+}{N}H_3$	769	63.7	201	13.3	$50._2$	38	0.76
$\overset{+}{N}H_3(CH_2)_8\overset{+}{N}H_3$	773	69.5	187	13.3	$46._9$	29	0.62
$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	778	75.3	172	13.3	$43._0$	16	0.37
			(*c*) alkyldiammonium hectorites (c.e.c. 91 meq 100 g^{-1})				
$\overset{+}{N}H_3(CH_2)_2\overset{+}{N}H_3$	769	34.8	240	12.2	$43._2$	49	1.14
$\overset{+}{N}H_3(CH_2)_3\overset{+}{N}H_3$	774	40.6	224	13.0	$51._8$	44	0.85
$\overset{+}{N}H_3(CH_2)^3\overset{+}{N}H_3$	779	46.4	208	[13.3]†	$51._9$	51	0.98
$\overset{+}{N}H_3(CH_2)_5\overset{+}{N}H_3$	783	52.2	192	13.3	$48._1$	49	1.02
$\overset{+}{N}H_3(CH_2)_9\overset{+}{N}H_3$	802	75.3	128	13.3	$32._0$	41	1.28

† Assumed value.

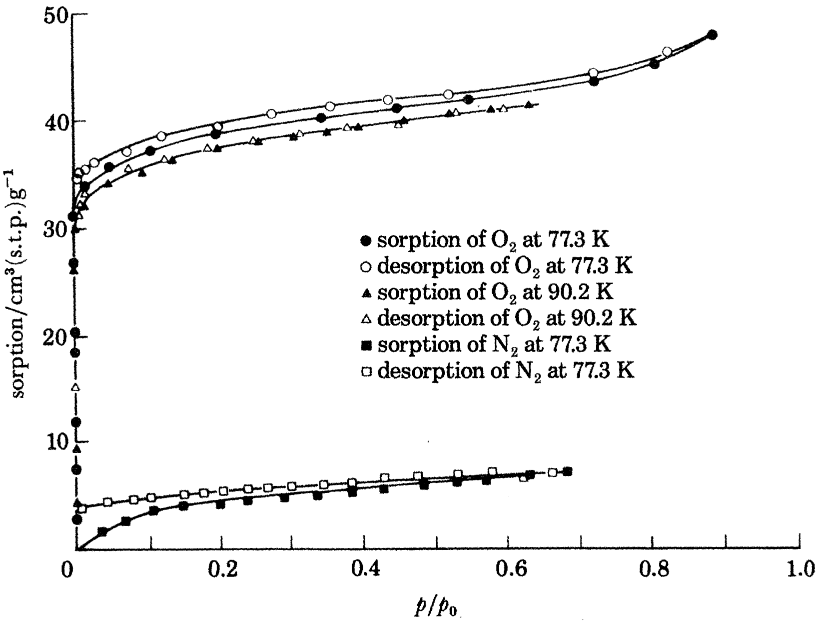


FIGURE 8. Isotherms for O_2 and N_2 at about 78 K and 90 K in $Co^{III}(en)_3$-FH150, showing very large difference in the uptake (Craven 1976; Barrer 1978).

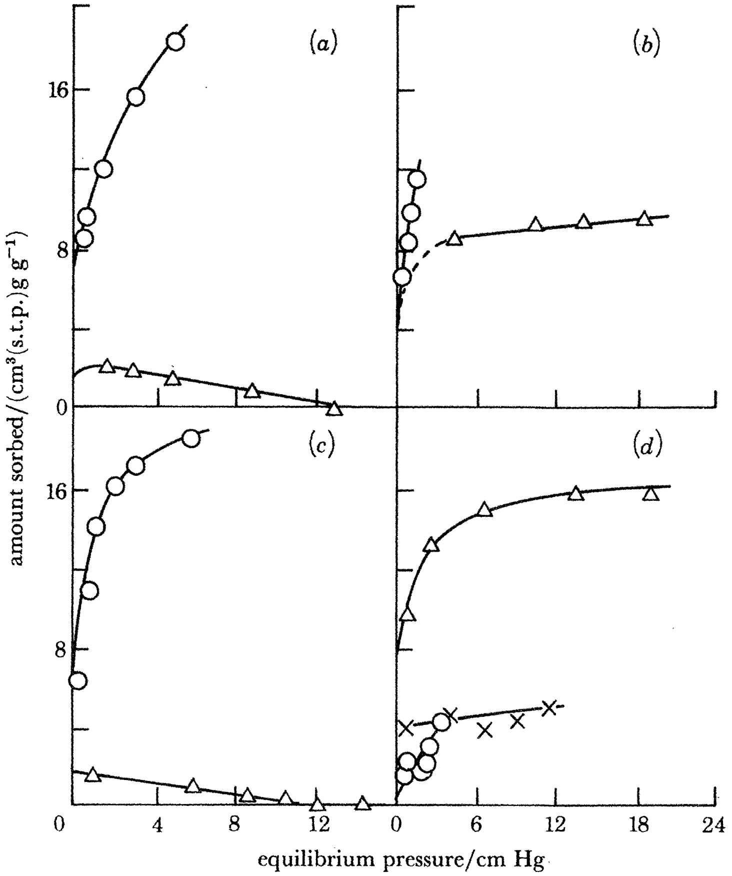
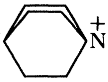


FIGURE 9. (*a*) and (*b*). Isotherms in $N(CH_3)_4$-montmorillonite for benzene (○) and *n*-heptane (△) from two mixtures with (*a*) 0.67 and (*b*) 0.30 mole fraction of benzene. (*c*) Isotherms for benzene (○) and cyclohexane (△) from a mixture with 0.67 mole fraction of benzene. (*d*) Cyclohexane isotherms from several mixtures with *n*-heptane with mole fractions 0.85 (○) 0.56 (×) and 0.16 (△) of *n*-heptane (Barrer & Perry 1961*b*). 1 mmHg = 133.322 Pa.

chromatographic columns at relatively high temperatures (Thielmann & McAtee 1975). Montmorillonite which had intercalated Λ-$[Ru(phen)_3]^{2+}$ (where phen is 1,10-phenanthroline) gave $d(001) = 18.0$ Å and so had a free distance of $(18.0-9.4) = 8.6$ Å. When dl-2,3-dihydro-2-methyl-5,6-diphenylpyrazine was sorbed into a short column of this complex and then progressively eluted with 1/2 (by volume) methanol water solvent a partial resolution of the dl-compound was achieved (Yamagishi 1983).

Permanently porous clay mineral sorbents are likely to attract growing interest. The globular ion H$\overset{+}{N}$$\overset{+}{N}$H exchanges with ions in montmorillonite and vermiculite (Mortland & Berkheiser 1976) and gives sorbents with free distances between lamellae of *ca.* 5.4 Å. These sorbents took up N_2, C_2H_6 and 2,4-dimethylpentane and had monolayer equivalent areas of 280 and 144 $m^2\ g^{-1}$ for the montmorillonite and vermiculite sorbents respectively. For some uses, however, organic and metal chelate cations in clay minerals have the disadvantage of thermal instability at high temperatures. Catalytic applications in particular could be limited by this instability to low temperature processes. It is however possible to produce rather stable permanently porous sorbents from smectites by exchanging into them the cations present in chlorhydrol solutions (Vaughan & Lussier 1980). These ions are thought to be $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and the resulting 'pillared' clays have an interlamellar free distance of about 9.6 Å. When the pillared clay mineral is heated with loss of zeolitic and hydroxyl water this difference is still about 9.4 Å. The product thus obtained sorbed *n*-butane, cyclohexane, CCl_4 and 1,3,5-trimethylbenzene but not 1,2,3,5-tetramethylbenzene or perfluorotributylamine. In another study (Ocelli *et al.* 1981) of a bentonite in which Na^+ was also replaced by oxy-aluminium cations the expanded clay mineral was reported to have a pore volume of 0.16 $cm^3\ g^{-1}$, a surface area of 250–300 $m^2\ g^{-1}$ and to be hydrothermally stable to 1000 °F. The micropore space was easily accessible to C_6–C_{10} *n*-paraffins and to substituted aromatics such as 1,3,5-trimethylbenzene.

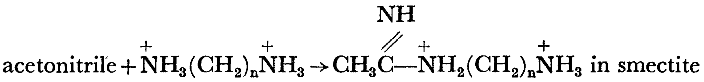
Montmorillonite and vermiculite have also been exchanged by $[SiA_3]^+$ where A is acetonylacetate. The exchange forms were hydrolysed at pH *ca.* 9 and heated in air at 100–600°. The product was reported as stable at high temperature and with silica groups separating the lamellae of the clay minerals (Pinnavaia *et al.* 1983).

5. Interlamellar reactions

Reactions which may occur in interlamellar spaces in clay minerals include the kinds given in table 7. The examples given are merely typical and the table could be much extended, both as regards the types of process catalysed and the number of examples of each type.

The substitution of Si^{4+} by Al^{3+} and of Al^{3+} by Mg^{2+} creates in smectites and vermiculites Lewis base sites, while in the interlamellar region there may be Lewis acid sites. Treatment with acids creates Bronsted acid sites. Accordingly catalytic properties in clay minerals are to be expected. An early use of acid clays was in catalytic cracking of petroleum but in this area such catalysts as well as alumina-silica cracking catalysts have been largely superseded by zeolite-based catalysts. Clay catalysts can also be used in dimerization of unsaturated fatty acids to dicarboxylic acids. Figure 10 (Weiss 1981) shows oligomerization reactions of oleic acid using a $(CH_3)_4N$-montmorillonite catalyst, as a function of charge density measured as $e/(Si, Al)_4O_{10}$ where e is the charge associated with the unit $(Al, Si)_4O_{10}$. The figure shows the influence of

TABLE 7. SOME TYPES OF REACTION PROMOTED BY CLAYS OR MODIFIED CLAYS

reaction type	example
cracking hydrocarbons	processing of petroleum
dimerization and oligomerization	oleic acid to di- and tri-carboxylic acids (Weiss 1981). Cyclohexene to oligomers (Barrer & Perry 1961*a*)
isomerization	*cis-trans* isomerization in oleic acid (Weiss 1981)
hydrogen transfer	oleic to di-unsaturated acid and stearic acid (Weiss 1981)
dehydration	NH_4-acetate in kaolinite → acetamide (Weiss 1981). NH_4-salts of aminoacids → peptides, in kaolinite and montmorillonite (Weiss 1981; Paecht-Horowitz *et al.* 1970)
oxidation	leuco-bases oxidized in copying papers in air or with other oxidant (Barrett *et al.* 1951)
esterification	ethylacetate from ethylene and acetic acid (Ballantine *et al.* 1981*a*)
lactonization	cyclooctene carboxylic acid → 1,4 and 1,3 lactones (Thomas 1982; Adams *et al.* 1982)
etherification	di(alk-1-yl)ether from alk-1-ene (Thomas 1982). Di(alk-1-yl)ethers from alkan-1-ols (Thomas 1982)
reduction	1-hexene $\xrightarrow{H_2}$ hexane with catalyst of Rh-phosphine-Na-hectorite complex (Raythatha & Pinnavaia 1983)
substitution	 acetonitrile $+\overset{+}{N}H_3(CH_2)_n\overset{+}{N}H_3 \rightarrow CH_3\overset{\overset{NH}{/\!/}}{C}-\overset{+}{N}H_2(CH_2)_n\overset{+}{N}H_3$ in smectite (Barrer & Millington 1967)
primary to secondary amines	$2R-CH_2NH_2 \rightarrow R-CH_2-NH-CH_2-R+NH_2$ (Ballantine *et al.* 1981*b*)

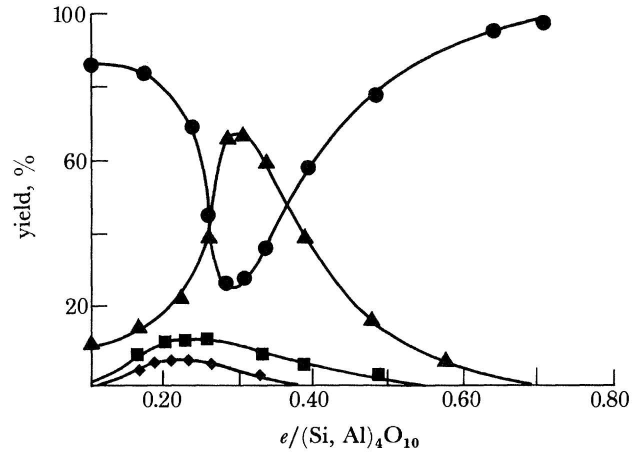


FIGURE 10. Oligomerization of oleic acid to di-, tri- and oligocarboxylic acids. $(CH_3)_4N$-montmorillonite is the catalyst and yield of each product is plotted against the charge density measured as the charge, *e*, per $(Si, Al)_4O_{20}$ unit. Starting material: oleic acid 98%; 0.5 gram catalyst per 100 ml of oleic acid (Weiss 1981). ● Oleic+stearic (C_{18}); ▲ dicarboxylic acids (C_{36}); ■ tricarboxylic acids (C_{54}); ◆ oligocarboxylic acids ($\geqslant C_{72}$).

charge density upon the behaviour. For $e > 0.6$ oligomerization was replaced by *cis–trans* isomerization and by hydrogen transfer to give di-unsaturated C_{18} acids and stearic acid (a redox-type process).

Technical development of copying papers illustrates the use of clay catalysts in oxidation. The front of the paper is filled with a montmorillonite containing some acid centres which catalyses oxidation of leucobases. The back of the paper has a coating containing leucobase and the pressure of writing forces contact between catalyst and leucobase. The oxidizing agent can be air (Barrett *et al.* 1951).

With reference to figure 10 further examples of the influence of charge density are of interest. Aniline with high charge density smectite readily oxidizes to a black 'polymer'; at medium charge densities it yields a red or blue 'oligomer'; and at low charge densities the aniline is not changed (Weiss 1963). Again, in the interlayer region of high charge density smectite liganded Co^{3+} is stable, while in low charge density smectite it is reduced to Co^{2+} (Weiss 1981):

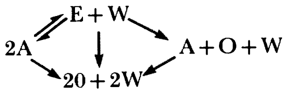
$$2[\mathrm{CoL}_n]^{3+} + 2\mathrm{H_2O} \rightleftharpoons 2n\mathrm{L} + 2\mathrm{Co}^{2+} + 2\mathrm{H}^+ + \mathrm{H_2O_2}.$$

The peroxide at once decomposes to $\mathrm{O_2}$ and $\mathrm{H_2O}$. As a final example one may consider the isomerization:

$$[\mathrm{Cr(H_2O]_5Cl}]^{2+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{Cl}^-,$$

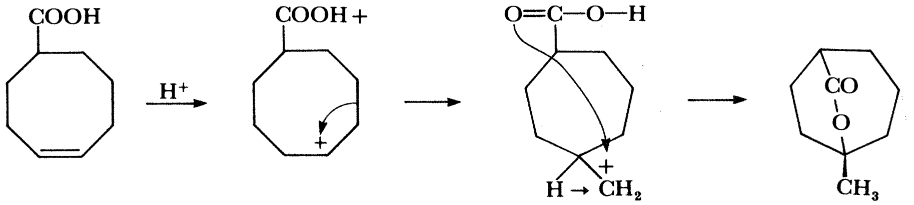
which is influenced by the charge density of the clay mineral. The trivalent interlayer cation is stable at high charge density but at low charge density the divalent cation is much preferred (Weiss 1981).

In a review of some reactions catalysed by clay minerals Thomas (1982) suggests that considerable parallels may exist between clay mineral and zeolite catalysts, an example being the scheme considered valid for several reactions catalysed by zeolites (Knözinger & Kohne 1966):



In this scheme A, E, O and W denote respectively alcohol, ether, olefine and water. The diagram summarizes reaction pathways without indicating mechanisms.

Mechanisms may in some processes be given a rational formulation in terms of carbenium ion intermediates, the proton being donated by Bronsted acid centres in the clay catalyst. As an example one may consider the lactonization reactions of cyclo-octene-5-carboxylic acid (Adams *et al.* 1982). Five lactones were produced, four of these being 1,4-cyclo-octanecarbolactone, 1,3-cyclo-octanecarbolactone; 3-methyl-3-cycloheptanecarbolacone and 4-methyl-4-cycloheptanecarbolactone. The carbenium ion mechanism for production of the last of these is representative (Thomas 1982):



However, mechanisms of acid clay catalyses cannot always be expressed unambiguously in

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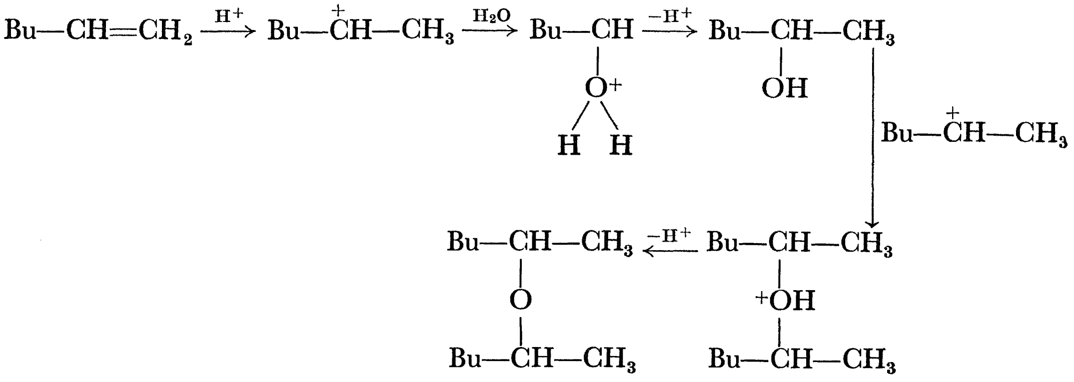
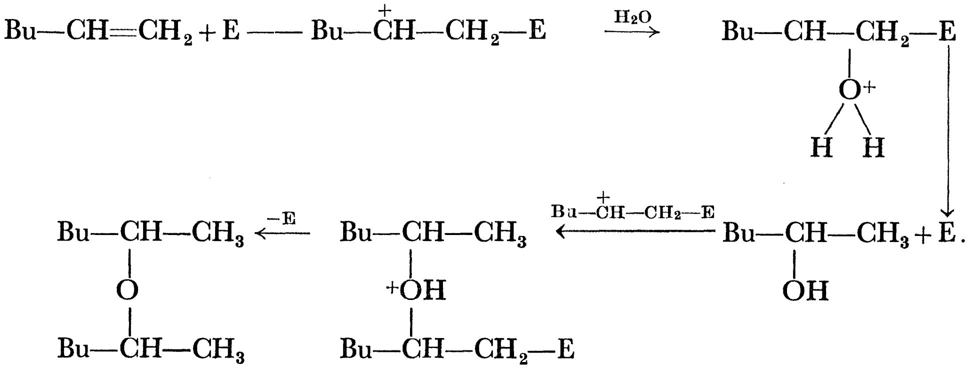
terms of carbenium ion intermediates. For example butyl ether formation from butene has been formulated by either of the pathways (i) Ballantine *et al.* 1981*b* or (ii) Adams *et al.* 1971:

(i)



(ii)



Mechanism (ii) involves the Lewis acid site E, i.e. an electron accepting site in the catalyst. In both mechanisms Bu denotes butyl.

Finally it is noted that the external surfaces of clay minerals, which are often of significant extent, may catalyse reactions so that independent evidence is required that the seat of reaction is in the interlamellar region. An example of catalysis involving the external surface only is provided by the polymerization of vinylethers using kaolinite at room temperature (R. M. Barrer and A. T. T. Oei, unpublished). Here there is no expectation of intercalation of the ether but the reaction occurred very vigorously as soon as the ether and kaolinite made contact.

6. CONCLUSION

This account of interlamellar sorption and catalysis by clay minerals demonstrates the notable richness in the phenomena observed and shows a still largely undeveloped potential for selective and molecular sieve separations, and catalyses which may as with zeolites be shape selective. The future of clay minerals in chemistry and chemical engineering looks very promising.

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Discussion

P. B. Tinker (*Rothamsted Experimental Station, Harpenden, Hertfordshire, U.K.*). Have you used water as guest molecule in the smectites with intercalated organic compounds? Natural clays must often contain some degree of intercalation; could you say anything about the effect this would have on water sorption? Is there any possibility that organic compounds could be lost from the clay if it expands on hydration?

R. M. Barrer. We have investigated only competitive sorption of two organic guest species, rather than water and an organic species. When one guest is used to displace a previously intercalated second guest the amount displaced will depend upon the relative vapour pressure (or solution concentration) of each guest, and the nature of the two guest species and hence the energy and type of bonding of each to the clay surfaces. In clay sorbents containing only small inorganic cations if the molecule first intercalated was large and polar (for example, a sugar, a peptide or a protein) displacement by water would be more difficult to achieve than for a small polar molecule such as methanol or ethanol. However, additional sorption of water could occur.