SURFACE PROPERTIES OF ALUMINO-SILICATES

by

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ABSTRACT

As an approach to reviewing the surface properties of alumino-silicates, this paper considers the relationships between constitution hydroxyls, surface hydroxyls, chemisorbed and physically adsorbed water molecules and exchangeable cations. One of the main characteristics of clay minerals is, indeed, the development of hydrated high surface area, electrically charged. For this purpose the surface topography, the origin of the electrical charge, and the properties of water molecules held by Van der Waals, or stronger forces are successively studied. Chemisorbed water molecules appear to have a higher than usual degree of dissociation; this phenomenon exerts a deep influence on surface properties such as surface electrical conductivity, chemisorption of ammonia and amines, and their transformation.

When surfaces are thoroughly dehydrated, constitution protons are probably delocalized in the oxygen framework and this delocalization process probably precedes dehydroxylation.

Dehydroxylation results in a partial or a total transformation of octahedral coordinated aluminum into four-fold coordinated atoms. Stresses arising from sharing adjacent octahedral edges are probably at the origin of the Lewis catalytically active sites.

The research reports reviewed are mainly those issued from the author's laboratories, or by his correspondents.

INTRODUCTION : SURFACE TOPOGRAPHY

IN order to understand the surface properties of clay minerals and synthetic amorphous alumino-silicates, it is of interest to give first the clearest possible representation of the surface of powdered samples. The interest will be mainly focused on the electrical charge distribution, and content and activity of hydroxyls. Properties of colloidal suspensions will not be considered here.

The correlation between specific surface area and chloride negative adsorption measurements on kaolinite suspensions (Schofield, 1947; Laudelout, 1957) proved that the surface density of charge may be calculated by dividing the C.E.C. (obtained at pH 7 by NH_4^+) by the B.E.T. specific surface of the sample if a homogeneous distribution is assumed. For clays characterized by expanding lattice, the surface area obtained from ethylene-glycol retention (Hendricks and Dyal, 1950) may be used for the same evaluation. The ratio C.E.C./surface area, calculated for a

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large number of different clays and gels, averages about 1.4 electrons per $m\mu^2$ (Fripiat, 1960; Greene-Kelly, 1962).

Besides electrical charges, alumino-silicate surfaces possibly bear OH radicals either bound to aluminum or silicon (silanol radicals). Among several proposed methods, surface OH may be evaluated by the reaction between CH_3Li and the "mobile" hydrogen; hydration water and total hydroxyl content can be determined by means of thermogravimetry and infra red spectroscopy (Uytterhoeven and Fripiat, 1962). Table 1 gives

TABLE 1.—HYDROXYL SURFACE DENSITY (PER $m\mu^2$) OBTAINED FROM THE CH_3Li METHOD AFTER OUT-GASSING AT 20°C, (CORRECTED FOR HYDRATION WATER)

Silica gels	Alumino-silicates
Xerogel: 4.5	Cracking catalyst: 9.3
Aerosil: 4.5	Na- and Ca-kaolinites: 3.4 (Busirian)
Ludox S.M.:2.3	

some results for silica gels (Uytterhoeven, Hellinckx and Fripiat, 1963), a cracking catalyst (Uytterhoeven and Fripiat, 1962) and a kaolinite (Uytterhoeven, 1963). Chemical and physical data for the samples reviewed here are given in the footnote.*

* Some chemical and physical data upon the samples reviewed in this paper are given hereafter.

Cracking catalyst: $Al_2O_3/Al_2O_3+SiO_2=0.13$; So (B.E.T.)$=478$ m² g⁻¹; C.E.C.$=150$ meq/100g.

Ludox S.M.: silica gel containing 1.65×10^{-4} Na equi. per gram SiO_2; So (B.E.T.)$=297$ m² g⁻¹.

Aerosil: very pure silica gel: Na content 10^{-6} Na equi. per gram SiO_2; So (B.E.T.)$=178$ m² g⁻¹.

Xerogel: silica gel containing 7.75×10^{-4} Na equi. per gram SiO_2; So (B.E.T.)$=420$ m² g⁻¹.

Camp Berteau Montmorillonite: SiO_2: 60.5 per cent; Al_2O_3: 20.75 per cent; Fe_2O_3: 2.88 per cent; Mg 3.81 per cent; H_2O: 8.82 per cent;
So (B.E.T.)$=106$ m²g⁻¹ (external surface area);
So (ethylene-glycol)$=725$ m² g⁻¹ (internal+external surface areas);
C.E.C.$=95$ meq/100g.

Kaolinite: (Yangambi, Congo Rep.):
SiO_2: 45.6 per cent; Al_2O_3: 39 per cent; Fe_2O_3: 0.6 per cent; H_2O: 14.5 per cent;
So (B.E.T.)$=42$ m² g⁻¹;
C.E.C.$=9.4$ meq/100g.

Kaolinite: (Busirian sediment, Congo Rep.): SiO_2: 50.8 per cent; Al_2O_3: 34.6 per cent; Fe_2O_3: 0.6 per cent; H_2O: 14.1 per cent;
So (B.E.T.)$=16$ m² g⁻¹;
C.E.C.$=5.5$ meq/100g.

Figure 1 gives the representation of the pore size distributions of silica gels (xerogel and aerosil) and cracking catalyst derived from their absorption data.
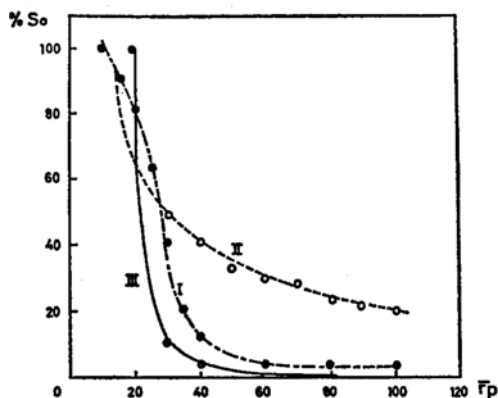
FIGURE 1.—Relative surface area developed by pores with radii wider than $\bar{r}p$ (in Å) for: I, xerogel; II, aerosil; III, cracking catalyst.

The total OH content (including water) of the cracking catalyst is exchangeable with D_2O at room temperature, while in kaolinite a very small fraction of the constitution water reacts under the same conditions (Fripiat and Gastuche, 1958). If these OH groups were located in the surface phase, they would have a surface density of 8 OH per $m\mu^2$.

Alumino-silicates and silica gels do not differ significantly by their OH densities but by the stability of their hydroxylic surface. This is expressed by Fig. 2 which shows the decrease of the relative OH surface contents obtained on long heating under vacuum at the temperature given on the abscissa. The only reasonable explanation which can be brought forward when considering the textural properties of the samples studied is that silanols are thermally more stable than hydroxyls bound to aluminum.

TABLE 2.—COMPARISON BETWEEN OH CONTENTS OF DIFFERENT SAMPLES, CATION EXCHANGE CAPACITY (C.E.C.) AND SPECIFIC SURFACE AREA (So)

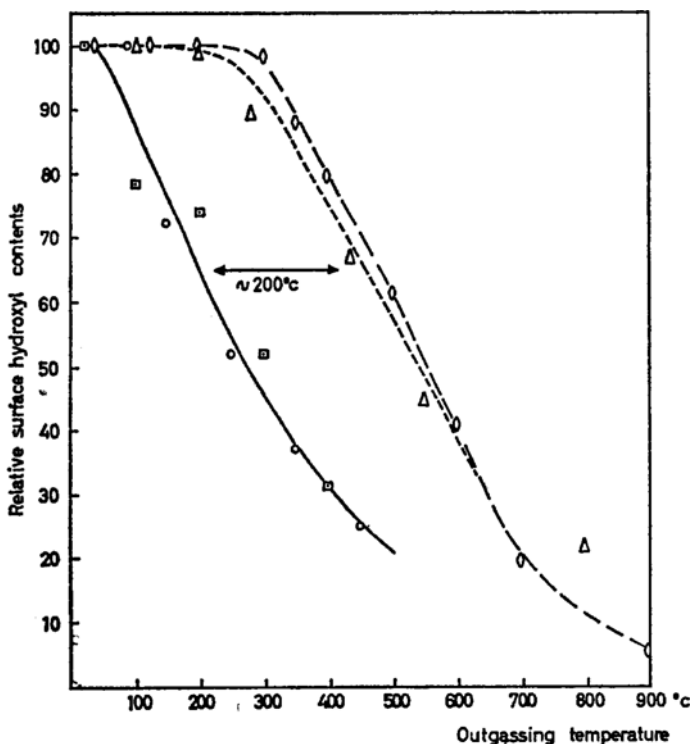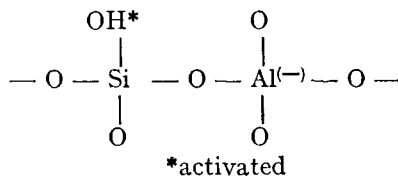| Sample outgassed at 20°	OH methylable: (CH_2N_2) $(10^{-3}$ mole g$^{-1})$	Surface OH (CH_3Li) $(10^{-3}$ mole g$^{-1})$	$\dfrac{\text{OH methylable}}{\text{surface OH}}$ (%)	C.E.C. (meq g^{-1})	So (B.E.T.) (m^2 g^{-1})
Cracking catalyst	1.51	8.0	18.9	1.5	478
Kaolinite (Yangambi)	0.088	0.23	38.3	0.092	42
Ludox S.M.	0.39	0.8	49	—	297

FIGURE 2.—Thermal stability of surface hydroxyls. Silica gels: △ xerogel, ◇ aerosil. Alumino-silicates: ⊙ kaolinite, ⊡ cracking catalyst.

Acid hydroxyls were tentatively determined by reaction with CH_2N_2 (Fripiat, Gastuche and Van Compernolle, 1954; Fripiat, 1957); some examples are given in Table 2.

The results thus obtained are questionable mainly because of a polymerization reaction of CH_2N_2 into polymethylene which can possibly occur on solid surfaces (Vivaldi, 1952). They may, however, demonstrate that in silica gel only a part of the OH surface reacts with CH_2N_2. If Ludox S.M. is outgassed at 100°C under vacuum, the ratio decreases to 25 per cent and remains almost constant even when the outgassing temperature reaches 500°C.

It follows that diazomethane does not allow a distinction between silanols and aluminum bound OH, but surprisingly enough (Fripiat, 1957 and 1960), when the methylable OH contents of kaolinite and cracking catalysts are compared to their C.E.C. (Table 2), the order of magnitude is similar, indicating a possible influence of the electrical charge on the mobility of the neighboring proton, as:

$$
\begin{array}{ccc}
\text{OH*} & & \text{O} \\
| & & | \\
- \text{O} - \text{Si} & - \text{O} - \text{Al}^{(-)} - \text{O} - \\
| & & | \\
\text{O} & & \text{O}
\end{array}
$$

*activated

We therefore formally classify hydroxyls into the species: OH bound to aluminum, to silicon, "acid" or "neutral" hydroxyls and so on.

The hydroxylic surface heterogeneity of silica gel may easily be shown by observing the isotopic exchange OH–OD for each of the three main components of the stretching vibration band in infrared adsorption records (Fripiat, Gastuche and Brichard, 1962). The first order law is obeyed but the rate constants, which can be measured separately, differ according to the OH species. Relative OH contents for aerosil are shown in Fig. 3 and the most probable diffusion models are indicated. At a relatively low tem-
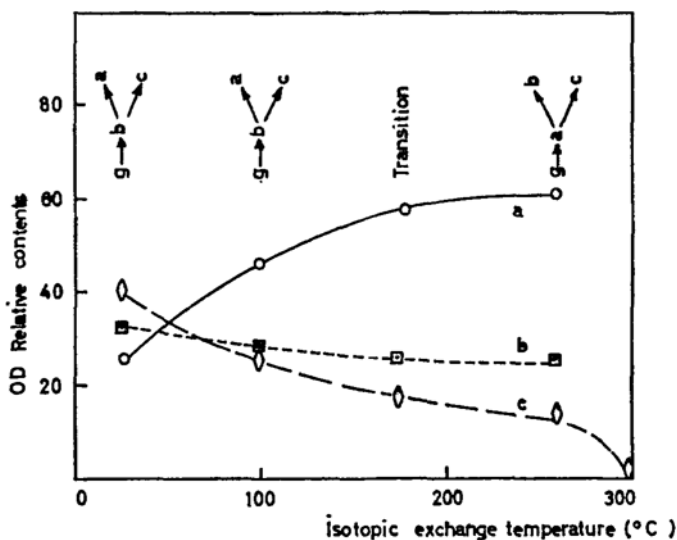

FIGURE 3.—Relative deuteroxyl contents for (a) isolated OD; (b) perturbed OD; (c) D_2O. The most probable diffusion mechanisms (OD–OH exchange) are indicated with respect to temperature, (g means "gas phase").

perature the privileged location of the bridged hydroxyls originates probably from the fact that they are the main (Zhdanov, 1958; Kiselev and Lygin, 1959) adsorption sites. According to Sidorov (Sidorov, 1956 and 1960), isolated or free OH only, in opposition to perturbed OH, undergo methylation when exposed to CH_3OH vapor at a rather high temperature.

ORIGIN OF THE ELECTRICAL CHARGE

The electrical charge is generally considered to originate from isomorphous substitutions in the lattice. The amount of four-fold coordinated aluminum in synthetic alumino-silicates depends upon (1) the composition, given by the ratio $Al_2O_3/Al_2O_3+SiO_2$, and (2) the pH of co-precipitation.

Influence of composition can be explained by the fact that so long as the aluminum content is low enough to allow its distribution in tetrahedra linked with four silica tetrahedra, the charge increases with the aluminum content. This has been pointed out in several papers (Tamele, 1950; Milliken, Mills and Oblad, 1950; Bosmans and Fripiat, 1958). Figure 4 reproduces such data from this laboratory.
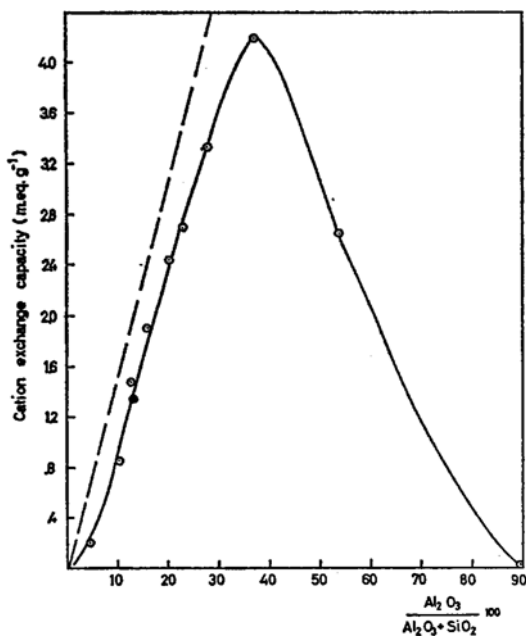

FIGURE 4.—C.E.C. of mixed silico-aluminic gels, co-precipitated at pH 8. The straight line represents the aluminum content in mole 10^{-3} g^{-1}.

In crystalline species, such as kaolinite, the charge attributable to four-coordinated aluminum originates from aluminum located at the edges only. Mild acid treatment (Gastuche, Delmon and Vielvoye, 1960) removes this external aluminum and there is a good correlation between the amounts extracted and the C.E.C. For two kaolinites, the specific surface areas of

which are 42.2 m² g⁻¹ and 16 m² g⁻¹, the ratios $\dfrac{\text{C.E.C.}}{\text{aluminum extracted}}$ are respectively 1.13 and 1.20.

The determination of aluminum coordination, based on the careful measurement of the Al Kα X-ray fluorescent line shift (White, McKinstry and Bates, 1958; De Kimpe, Gastuche and Brindley, 1961), has been applied to the measurement of the Al^{IV}/Al^{VI} relative contents of alumino-silicic gels freshly precipitated in the 2–8 pH range or aged for one to three months in the mother solutions. In all these samples, the $Al_2O_3/SiO_2 + Al_2O_3$ percentage was kept constant at 29 per cent. The octahedral aluminum relative contents are highest at low pH's of precipitation (Fig. 5a) and the C.E.C. varies accordingly (Fig. 5b).
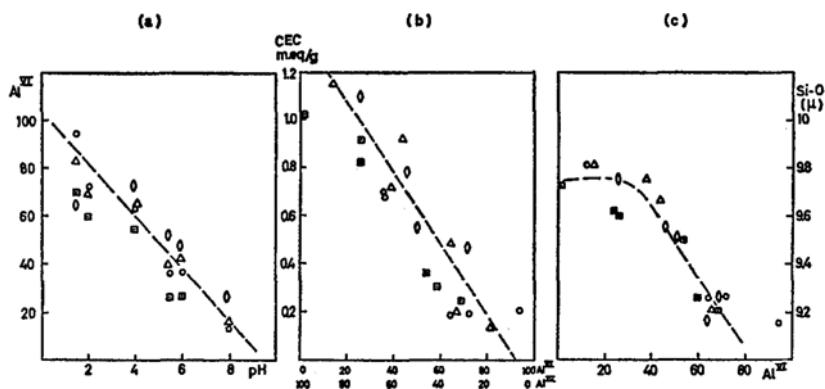

FIGURE 5.—(a) Al^{VI} relative content versus precipitation pH, (b) C.E.C. versus relative Al^{VI} or Al^{IV} content and (c), SiO stretching band wavelength versus relative Al^{VI} content, for : ⊙ freshly precipitated, ⊡ one month aged, ◇ two months aged and △ three months aged alumino-silicic gels. All gels had compositions which approximated to $Al_2O_3/Al_2O_3 + SiO_2$ = 29 per cent.

The reason why a low pH induces the octahedral coordination of aluminum is still an open question. According to Iler (1955), the tetrahedral form of aluminum is unstable when the balancing cation is exchanged by H_3O^+. The conversion of Al^{IV} into Al^{VI} must necessarily increase the gel hydroxyl contents: it has been effectively proved elsewhere that the ratio OH/H_2O decreases with increasing C.E.C. (Gastuche and De Kimpe, 1959), the cations entering the lattice with their hydration water.

Figure 5c shows an interesting correlation between the wavelength of the main Si–O stretching vibration and the relative Al^{VI} contents of these gels. The progressive introduction of aluminum tetrahedra into the silica frame-

work lowers noticeably its rigidity and the Si–O stretching frequency (De Kimpe, 1961; Fripiat and Gastuche, 1963). The same observation has been made in micas and chlorites (Stubican and Roy, 1961; Lyon and Tuddenham, 1960).

In unheated crystalline alumino-silicates, such as montmorillonite, free protons may subsist as exchangeable cations but a rapid aluminization process precludes the storage of the clay under the H-form because of the H_3O^+ exchange by $Al(OH)_6^{3+}$ (Paver and Marshall, 1934; Eeckman and Laudelout, 1961). In non-aqueous solvent this reaction rate is slower.

In the special case of kaolinite, however, the C.E.C. cannot be entirely attributed to isomorphous substitutions. It is observed that the C.E.C. is greater at high rather than at low pH's (Schofield, 1956): this variation is shown in Fig. 6 (Ekka and Fripiat, 1957). When the amount of methylable hydroxyls (by CH_2N_2) is measured for vacuum-dried samples, a lowering

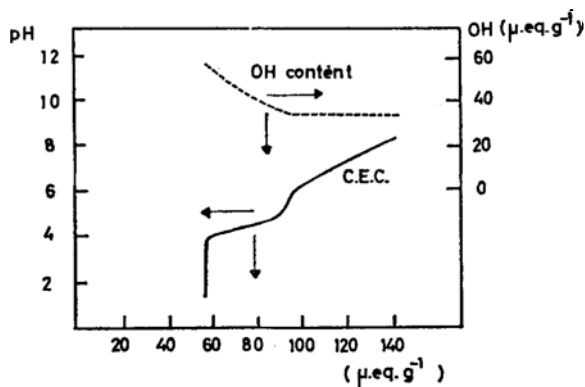FIGURE 6.—Variation of the C.E.C. of kaolinite and its "acid" OH content (CH_2N_2) with respect to equilibrium pH.

of the methylable OH contents is observed between the two levels corresponding respectively to the high and to the low C.E.C. This probably reveals a dissociation of silanols at high pH's and an exchange of their protons by metallic cations.

RESIDUAL WATER AND PHYSICALLY ADSORBED WATER

Since hydroxyls specialized as water molecules subsist under vacuum, it must be accepted that the forces involved in this adsorption are stronger than the Van der Waals forces. Hydrogen bonding between surface hydroxyls or surface oxygen atoms and water molecules can provide the required additional energy:

Three arrangements, (a), (b), and (c) may be considered:

(a)   (b)   (c)
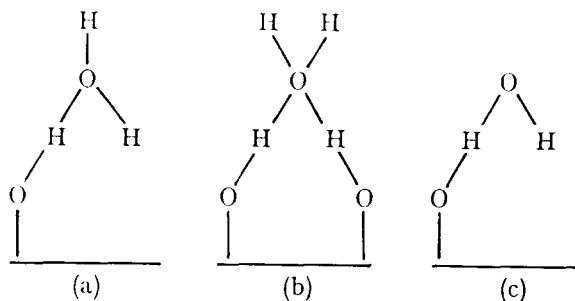
On hydrated silica surfaces the most favorable situation is represented by (b), while on dehydrated surfaces adsorption sites, as (c), gain importance. The hydroxyls represented by (a) are less active, since their methylation does not strongly affect the water adsorption capacity (Sidorov 1956 and 1960).

The presence of electrical charges in mixed gels introduces new possibilities for water retention. Let us compare from the viewpoint of water molecules content a pure silicic gel and an amorphous alumino-silicate.

Data of Table 3 clearly show that in spite of its less stable hydroxylic surface (Fig. 2), a cracking catalyst remains more hydrated than a silica gel in a large temperature range.

TABLE 3.—RELATIVE AMOUNTS OF WATER MOLECULES LEFT ON THE SURFACE TO THE NUMBER OF SURFACE HYDROXYLS (CH_3LI) WITH RESPECT TO THE OUTGASSING TEMPERATURE

Silica gel aerosil		Cracking catalyst ($Al_2O_3/Al_2O_3+SiO_2=13\%$)	
Temperature (°C)	H_2O/surface OH (%)	Temperature (°C)	H_2O/surface OH (%)
20	28	20	50.5
60	20	100	52.7
100	16	200	25.6
140	12	300	22.4
200	4.5	∼400	0
240	2.4		
∼300	0		

This might be accounted for by (1) a higher OH surface density which makes the coupling of two OH with a water molecule more probable, (2) a complexing effect of the charge balancing cations, (3) different pore size distributions. Aerosil has a lower percentage of narrower pores than a

cracking catalyst. Diffusion of water molecules may consequently be more delayed in this last case.

In clay minerals montmorillonite and vermiculite the complexing power of an exchangeable cation is the determining factor for the amount of residual water, as emphasized in numerous papers (Mering, 1946). Dehydration processes at atmospheric pressure have been followed by X-ray diffraction and infrared spectroscopy (Fripiat, Chaussidon and Touillaux, 1960). The main results are summarized in Fig. 7.
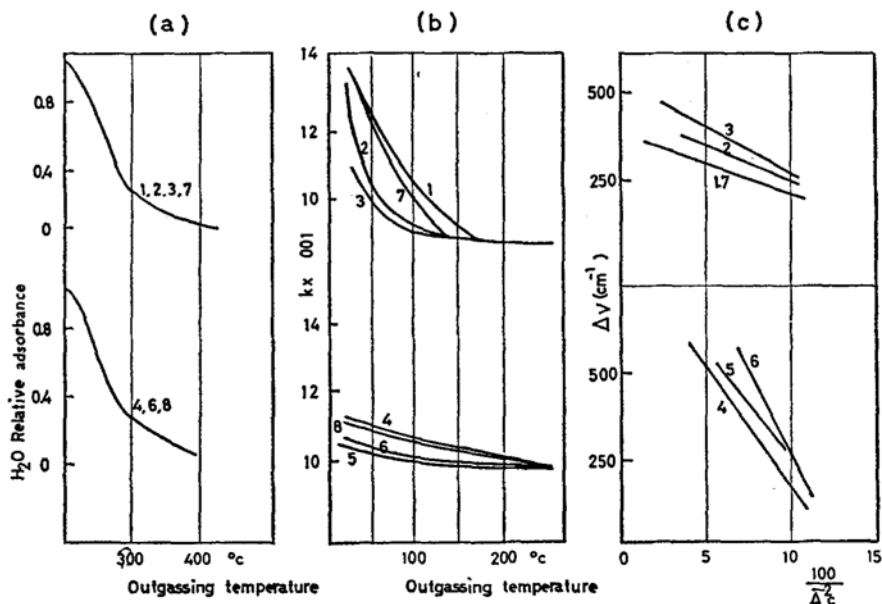

FIGURE 7.—Variation of the relative adsorbance of the angular vibration band of hydration (a) water with respect to temperature; (b) change of d 001 spacing against temperature and, (c) frequency shift (see text) for 1, Li-montmorillonite; 2, Na-montmorillonite; 3, K-montmorillonite; 7, Sr-montmorillonite; 4, Sr-vermiculite; 5, Li-vermiculite; 6, K-vermiculite; 8, Na-vermiculite.

The progressive dehydration of homoionic montmorillonites and vermiculites is followed by plotting the relative adsorbance of the H_2O deformation vibration band with respect to the outgassing temperature (Fig. 7a). The dehydration processes of different homoionic samples appear to be the same although the absolute retention levels differ, as observed from the variations of the $00l$ spacings (Fig. 7b).

Dehydration results in a contraction of the interlamellar space thus changing the electrical field F acting upon the residual water molecules Let $\vec{F_1}$ and $\vec{F_1'}$ be the field contributions of the negative charges brought

by the sheets and $\overrightarrow{F_2}$ the positive contribution of the exchangeable cations $(\overrightarrow{F} = \overrightarrow{F_1} + \overrightarrow{F_1'} + \overrightarrow{F_2})$. $\overrightarrow{F_1} + \overrightarrow{F_1}$ decreases when two adjacent sheets approach each other. Strengthening of hydrogen bonds would shift the OH stretching of H_2O towards lower frequencies. In fact the opposite effect is observed, as shown by the linear decrease of Δv with respect to $100/\overline{\triangle c}^2$ (Fig. 7c).[*]

This may be accounted for by introducing into the Morse function of the oscillator a perturbation due to a positive field as proposed by Cogeshall (1950):

$$\Delta v = -\frac{3qF}{4\pi c(2\mu)^{\frac{1}{2}} D^{\frac{3}{2}}}$$

where q is the charge of the dipole, c the light velocity, μ the reduced mass, D the dissociation energy and F the field component along the OH dipole direction.

Since the *00l* sequences of X-ray reflections are irrational during the dehydration process, the relationship can be applied only as a rough approximation. Nevertheless, the linear relationships of Fig. 7c show (1) that the various cations have a stronger or a weaker action according to the nature of the clay minerals (2) that the resulting field between vermiculite sheets is stronger. This is probably due to a higher charge density.

The interaction between water and charged surfaces of montmorillonite may also be studied by following the conductivity σ of clay plugs as a function of their adsorbed water contents. Unpublished data, obtained by G. Poncelet of this laboratory, on Ca- and Na-montmorillonites show an exponential relationship of the type:

$$\sigma = \sigma^* . \, e^{\,\theta}$$

where θ is the coverage degree of the surface by water molecules. The exponential factor c is always lower for H_2O than for D_2O.

The following arguments are in favor of the hypothesis that the charge carriers are protons coming from a partial dissociation of the hydration water.

If metal cations were the charge carriers, the exponential relationship between σ and θ would be difficult to explain. The increasing water adsorption "opens" successively interlamellar spaces, following an "all or nothing" mechanism. By assuming that the expansion of interlamellar space allows cations to diffuse, a more or less linear relationship would exist between σ and θ.

On the other hand if the charge carriers are protons coming from a water dissociation (or predissociation) process induced by the polarizing

[*] $\triangle v$ is equal to the frequency of free OH stretching (i.e. 3750 cm^{-1}) minus the actual one. $\triangle c$ is the width of the interlamellar space $(d\ 001+9.6$ Å$)$.

action of exchangeable cations, a "chain" diffusion mechanism takes place. A proton interacts with free sp^3 orbitals of oxygen atoms belonging either to the clay surface or to water molecules. Transmission from a free to another orbital occurs by successive tunelling and slow rotation of water molecules (Conway, Bockriss and Linton, 1956). Such a mechanism requires a continuous structure of the oxygen chains and explains the exponential law. The higher "c" value observed upon D_2O adsorption also becomes understandable.

Recent proton magnetic resonance results also suggest that water adsorbed by montmorillonite has a higher than usual degree of dissociation (Pickett and Lemcoe, 1959; Ducros and Dupont, 1962): the average life of a proton in any particular molecule is so short that a degree of ionization at least 1000 times higher than normal is probable.

All these considerations emphasize the importance of the exchangeable cation-adsorbed water association, since it is believed that it results in a partial dissociation. It is therefore worthwhile to know the "hydration numbers" of exchangeable cations.

Results obtained from different procedures for kaolinite follow the expected trend, as shown by Table 4.

Table 4.—Cation Hydration Numbers on Kaolinite Surface

Sample	Gastuche and Fripiat (1958)	Uytterhoeven (1963)	Keenan, Mooney and Wood (1951)
Li-kaolinite	2.7	2.1	0
Na-kaolinite	1.6	1.7 — 2.1	2.4
K-kaolinite	1.7	2	1.6
Mg-kaolinite	10.0	4.9	—
Ca-kaolinite	7.8	4.3 — 4.9	10

It is of interest to point out that cations associated with clays without internal surfaces, such as kaolinite, dehydrate at a much lower temperature than those in montmorillonite where OH's specialized as water molecules subsist up to 400°C (Fig. 9a).

When physical adsorption of water occurs on outgassed kaolinite surfaces (Fripiat and Dondeyne, 1960) the film is first made of molecules which probably build sorts of "icebergs" around partially or fully dehydrated cations.

As cation dehydration occurs around 50–60°C a distinction must be drawn between results obtained after outgassing the samples under vacuum at 20 or 70°C. Moreover the residual hydration for Ca^{2+} is higher than for Na^+, according to Table 4.

At low fractions of surface coverage ($\theta < 0.2$), water molecules adsorbed by Na-kaolinite outgassed at either 20 or 70°C, do not have any degree of freedom (see data on Table 5). For Ca-kaolinite outgassed at 20°C, additional adsorbed molecules, more weakly bound than the ones left on the surface after outgassing, keep one degree of rotation but cannot move freely upon the surface.

TABLE 5.—PHYSICAL ADSORPTION OF WATER ON KAOLINITE SURFACE

Pretreatment: outgassing temperature (under vacuum)	Coverage degree	$-\triangle S$: entropy loss derived from calorimetric data ($\triangle H$) and adsorption isotherms ($\triangle F$) at 20°C $\triangle S_{th}$: theoretical values from statistical thermodynamics for given degrees of freedom of adsorbed molecules					
	sample	Na-kaolinite			Ca-kaolinite		
	θ	$-\triangle S$	$-\triangle S_{th}$	Interpretation	$-\triangle S$	$-\triangle S_{th}$	Interpretation
20°C	0.2	47.2	44.8	translation 0 rotation 0	40.9	41.9	translation 0 rotation 1
	0.5	40.2	41.9	translation 0 rotation 1	32.7	28.7	translation 2 rotation 1
	0.9	30.9	27.2	translation 2 rotation 1	22.3	20.0	translation 2 rotation 3
70°C	0.2	47.2	44.8	translation 0 rotation 0	45.6	44.8	translation 0 rotation 0
	0.5	41.3	41.9	translation 0 rotation 1	36.9	31.4	translation 0 rotation 0
	0.9	29.8	27.2	translation 2 rotation 1	25.1	27.2	translation 2 rotation 1

This rotational degree disappears for molecules adsorbed by fully dehydrated Ca-kaolinite.

With increasing coverage in Na-kaolinite, one rotational and one translational degree of freedom appear successively. This gain in degrees is delayed for Ca-kaolinite outgassed at 70°C as a higher hydration number is required by divalent cations. It is only at $\theta \simeq 1$ that bidimensional translation does occur in both samples.

When physical adsorption of water occurs on powdered glass surfaces the entropy loss indicates that molecules build an immobile film up to $\theta = 1$. This clearly appears from unpublished data obtained in this laboratory by A. Jelli* and reproduced in Table 6.

TABLE 6.—ENTROPY LOSS OF WATER MOLECULES ADSORBED AT 38°C ON
GLASS SURFACES: $-\triangle S$: EXPERIMENTAL; $-S_{th}$: THEORETICAL

θ	$-\triangle S$	$-\triangle S_{th}$ (translation O) (rotation 1)
0.2	47.6	46.8
0.4	46.0	45.8
0.6	44.9	45.3
0.8	43.8	44.7

A vibrational degree of freedom with respect to the adsorption site has been taken into account in the computation of $\triangle S_{th}$

On both kaolinite and glass surfaces, hydroxyls behave as barriers opposing the mobility of water molecules.

THE ACID CHARACTER OF HYDRATED OR PARTIALLY HYDRATED SURFACES

Interaction of ammonia with the expanding lattices of montmorillonite and vermiculite involves factors such as the competition between water and ammonia in the coordination sphere of exchangeable cations, the relative affinity of water and ammonia for complexing these cations and the proton affinity of NH_3 molecules (Mortland, Fripiat, Chaussidon and Uytterhoeven, 1963).

In acid montmorillonites, saturated partially by protons and aluminum cations, NH_3 reacts with protons to form ammonium. In base saturated montmorillonite and vermiculite, ammonia would form hydrates or react with protons coming from water dissociation. Whatever the case, adsorption of ammonia expands the montmorillonite lattice, as shown in Fig. 8, while vermiculite does not swell. Moreover when hydrated Ca-vermiculite is exposed to NH_3, an almost complete contraction occurs, indicating the removal of water molecules. In spite of the absence of swelling, chemical analysis indicates a high level of ammonia retention in outgassed vermiculite. Expressed in equivalents, this residual amount is of the order of magnitude of one-half of the C.E.C. of the mineral.
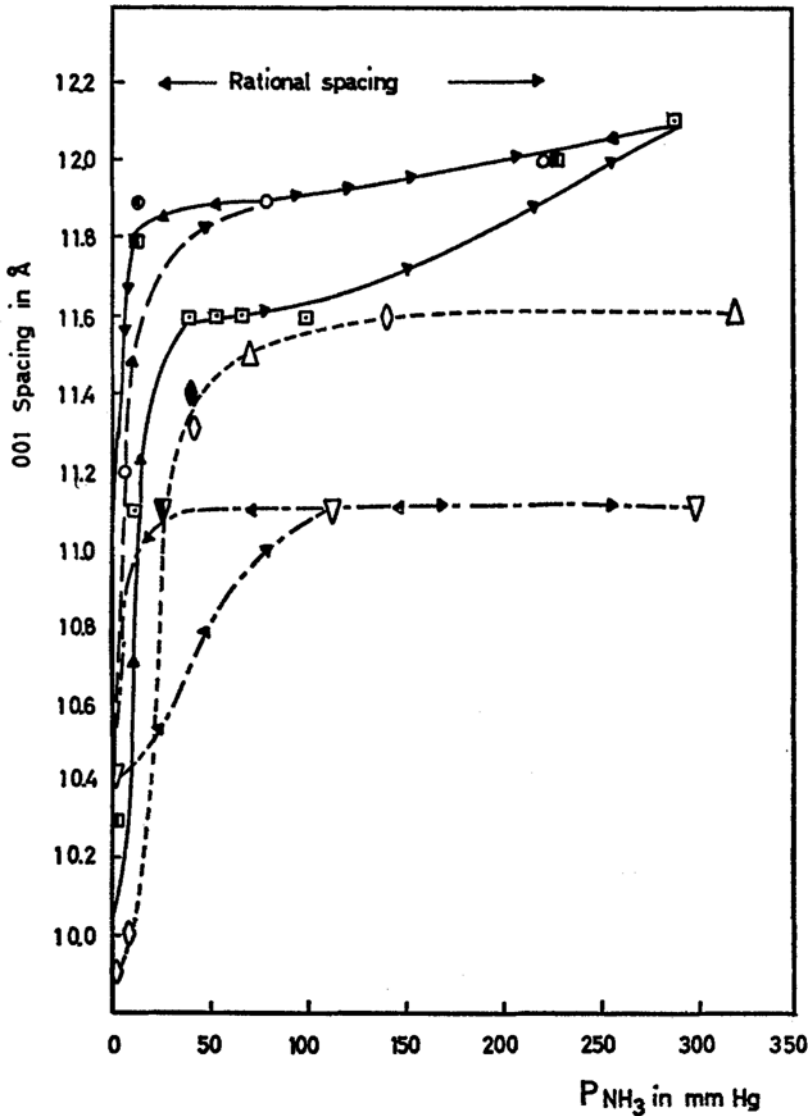
FIGURE 8.—*00l* spacing vs. pressure of NH_3 in mm Hg for H-montmorill-onite: O ads., ◉ desorp.; Ca-montmorillonite; ⊡ ads., ▉ desorp.; Na-montmorillonite; ◇ ads., ◆ desorp.; K-montmorillonite; △ ads.; Cs-montmorillonite; ▽ ads., ▼ desorp.

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In 100 g acid montmorillonite, outgassed at 100°C under vacuum, 83 millimoles of NH_3 remain adsorbed; about 20 to 50 millimoles of NH_3 are retained by the Na- and Ca-montmorillonites outgassed for a long time at 20°C.

In Figs. 9 and 10, infrared spectra, in the 3 and 6–7μ regions, of both H- and Ca-montmorillonites treated by NH_3 are compared. Besides the lattice OH stretching and the H_2O deformation bands, the main spectral features are essentially the same as the ones observed in montmorillonite saturated by NH_4Cl in solution (Table 7).

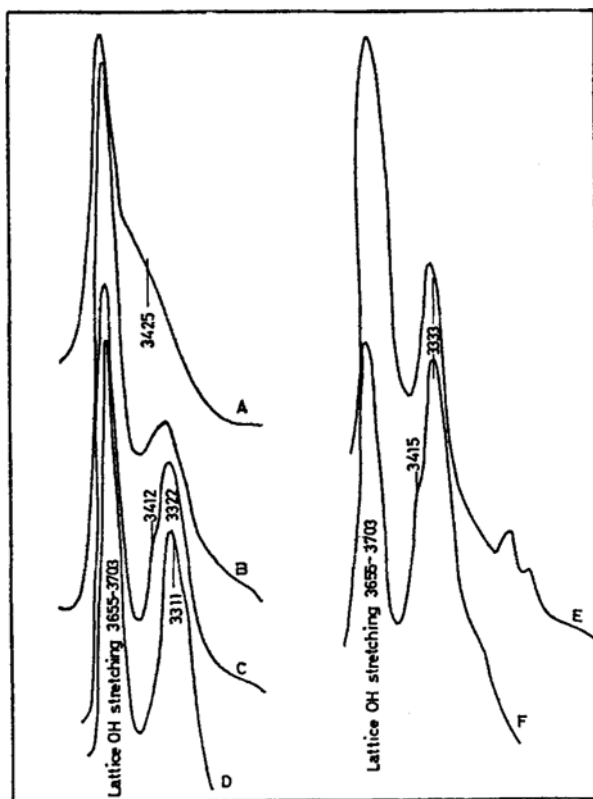When compared with crystalline ammonium halides, the shift of ν_3 and

FIGURE 9.—Infrared spectra in the 3μ region. Adsorbance vs. linear wavelength scale H-montmorillonite: A, outgassed at 120°C; B, exposed to 40 mm NH_3 and outgassed at 30°; C, exposed to 266 mm NH_3 and outgassed at 30°; D, outgassed at 130°. The shoulder around 3412–3426 cm^{-1} is attributed to OH stretching of residual water. Ca-montmorillonite: E, exposed to 10 mm NH_3 and outgassed at 220°; F, exposed at 300 mm NH_3 and outgassed at 30°. E and F result from different films.
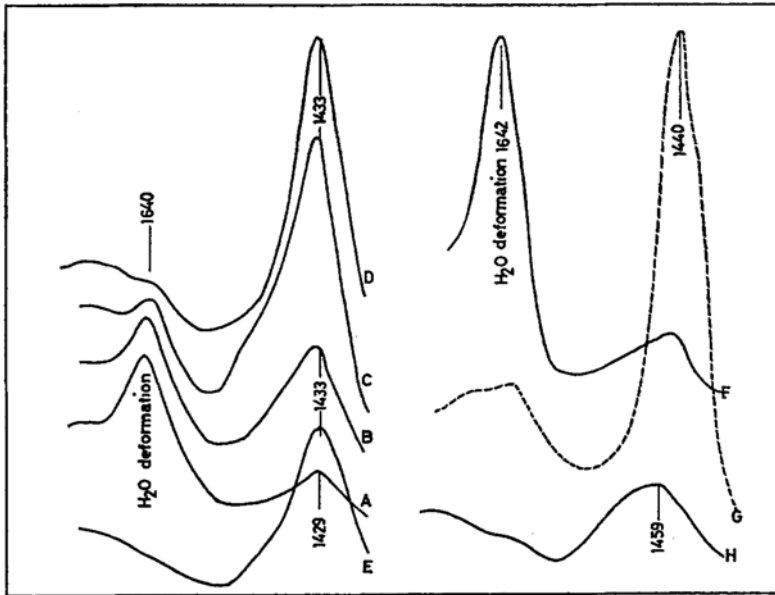
FIGURE 10.—Infrared spectra in the 6–7μ region. Adsorbance vs. linear wavelength scale. H-montmorillonite: A, outgassed at 120°, B exposed to 40 mm NH$_3$ and outgassed at 30°; C, exposed to 266 mm NH$_3$ and outgassed at 30°; D, outgassed at 130°; E, outgassed at 250°. Ca-montmorillonite: F, exposed to 57 mm NH$_3$ and outgassed at 30°; G, exposed to 300 mm NH$_3$ and outgassed at 30°; H, outgassed at 240°.

TABLE 7.—MAIN SPECTRAL FEATURES OBSERVED IN NH$_4$-MONTMORILLONITE AND IN NH$_3$ TREATED H- AND CA-MONTMORILLONITES.

	v_3 (cm^{-1})	v_4 (cm^{-1})
H-montmorillonite treated by NH$_3$	3311	1433
H-montmorillonite treated by ND$_3$	2469	—
Ca-montmorillonite treated by NH$_3$	3333	1459
Ca-montmorillonite treated by ND$_3$	2481	—
NH$_4$-montmorillonite	3280	1440
NH$_4$Cl (solid)	3138	1403
ND$_4$Cl (solid)	2350	1066

v_4 towards higher values indicates a state of greater freedom for chemisorbed NH_4 or ND_4 species. This agrees with the predicted shift for $NH_4{}^+$ bound to a less polarizable anion (Mathieu and Poulet, 1960).

It must be recalled that ammonia dissolved in water does not show the spectral characteristics of ammonium: the 1400 cm^{+1} deformation band does not appear (Waldron and Hornig, 1953).

Therefore data of Figs. 9 and 10 suggest the existence of protons both in acid and base saturated clays which convert adsorbed NH_3 to $NH_4{}^+$. The same phenomenon occurs even after outgassing the samples at about 200°C under vacuum. There is no evidence of trapped NH_3 species even when the residual NH_3 pressure is 1 mm Hg at 20°C but spectral characteristics of NH_3 are observed after adsorption at low temperature ($\simeq$ -180°C): a new NH stretching band appears at 3390 cm^{-1} under these conditions.

It could be assumed that constitution hydroxyls provide the proton attracted by adsorbed NH_3, but the kinetic study of isotopic exchange shows that the reaction rate between chemisorbed ND_3 and lattice OH becomes appreciable above 200° only. Thus, the following reaction must occur to some extent:

$$(H_2O)_{ads} + NH_3 \rightarrow NH_4{}^+ + OH^-$$
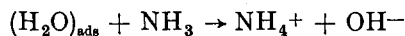
Two sets of observations substantiate this viewpoint:

(a) The adsorbance of the residual H_2O deformation band is proportional to the adsorbance of $NH_4{}^+$ deformation band (Fig. 11). When higher chemisorption levels are obtained by increasing NH_3 pressure before

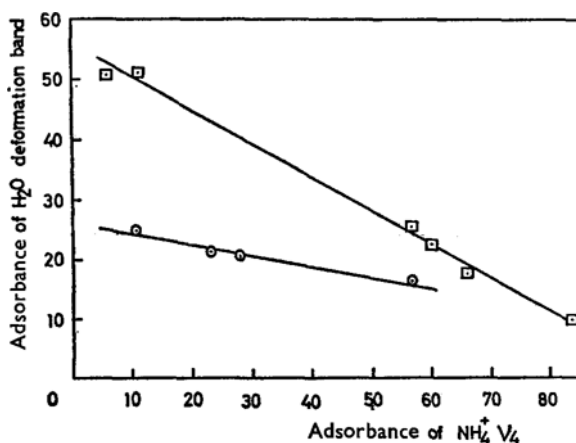FIGURE 11.—Adsorbance of H_2O deformation band against adsorbance of $NH_4{}^+$ deformation band for Ca-montmorillonite (□) and H-montmorillonite (○).

TABLE 8.—AMINES. ADSORPTION BY MONTMORILLONITES

	Complexes	Millimoles adsorbed at saturation per 100 g montmorillonite	Average c spacing and interlamellor spacing $\overline{\Delta c}$ (in kx)	Probable orientation of the organic chain with respect to the 00l planes	Infrared spectral characteristics (δ = deformation vibration band)
Class I — 1st group	H-mont. { +BA / +PA }	100 / 100	$\bar{c}=12.8\ \overline{\Delta}\ c=3.2$	perpendicular	(1) δ (NH$_3{}^+$) sym. present and not shifted
	Na-mont. { +BA / +PA }	20 / 35	irrational 001 series	—	(2) δ (NH$_3{}^+$) asym. probably present but overlapped by (H$_2$O)
	Ca-mont. +PA	87	irrational 001 series		
Class I — 2nd group	H-mont. { +EDA / +PDA }	50 / 50	$\bar{c}=12.2\ \ \Delta c=2.6$	parallel	(1) δ (NH$_3{}^+$) sym. present but shifted toward higher frequencies ($\Delta\nu=20$–30 cm^{-1}) (2) δ (NH$_3{}^+$) asym. probably present
Class II	H-mont. { +EDA / +PDA }	150 / 150	$\bar{c}=12.8\ \ \Delta\bar{c}=3.2$	perpendicular	(1) δ(NH$_2$) present
	Na-mont. { +EDA / +PDA }	110 / 110	$\bar{c}=12.8\ \ \Delta\bar{c}=3.2$	parallel	(2) δ (NH$_3{}^+$) sym. and asym. absent

N.B.: BA: butylamine; PA: propylamine; EDA: ethylenediamine; PDA: propylene diamine.
Freeze dried montmorillonites are treated by benzenic solution of amines. Samples are washed with benzene and vacuum dried for 24 hr at room temperature before use.

outgassing (probably because the increased pressure increases the rate of NH_3 diffusion into the lattice), the amount of residual water decreases. This might possibly be accounted for by the removal of H_2O by NH_3 but the slope of the linear relationship is much steeper for Ca-montmorillonite (where water is the only likely proton source) than for H-montmorillonite where exchangeable protons react with ammonia. For Ca-vermiculite the same kind of relationship holds between the adsorbance of water and NH_4^+ deformation bands.

(b) The amount of chemisorbed ammonium is higher the more hydrated the exchangeable cation.

When H-montmorillonite is treated in benzenic solutions by amines such as butyl- and propyl-amine or by diamines such as eythlene- or propylene-diamine, the transformation into alkylammonium or diammonium cation is observed (Fripiat, Servais and Leonard, 1962). Al-montmorillonite reacts in the same way, which evidences the dissociation: $Al(H_2O)_6^{3+} \rightarrow [Al(OH/_3(H_2O/_5]^{2+} + H^+$. The amount of a monoamine adsorbed and transformed into monoalkylammonium cation is stochiometrically equivalent to the C.E.C. of the clay mineral. Diamines are taken either stochiometrically or in excess according to the concentration of the benzenic solutions. X-ray, infrared and chemical data of these processes are summarized in Table 8.

Two classes of complexes are differentiated on the basis of these observations. Complexes obtained from interaction between monoamines and H (or Al)-montmorillonites and Na- or Ca-montmorillonites fall into a first group of class I characterized by perpendicular orientation of the aliphatic chain with respect to the $00l$ planes and by the two deformation vibration bands of $-NH_3^+$. The symmetrical deformation band is not shifted with respect to the frequency observed in corresponding pure chloride.

Acid montmorillonite in which the C.E.C. is saturated by diamines, forms a second group of class I complexes characterized by the parallel orientation of the aliphatic chain with respect to the $00l$ planes and by a rather appreciable shift of the symmetrical deformation band of $-NH_3^+$.

When the chain lies parallel to the $00l$ planes, the three hydrogen atoms of $-NH_3^+$ are in intimate contact with the mineral surfaces and this might explain the shift of the symmetrical "breathing" deformation frequency. In base saturated montmorillonites, the partial transformation of monoamine into monoalkylammonium, though of another order of magnitude than that observed for acid clays, is comparable to the one observed for NH_3 under similar conditions.

Parallel orientation of alkyldiammonium probably results from a mutual and particular accommodation of the charge distribution upon the clay surface and the distance between the two $-NH_3^+$ radicals as shown by Fig. 12. Alkylmonoammonium cation, held by one point only, is free to orientate such as to realize the highest packing.

Class II complexes result from the adsorption of an excess of diamines
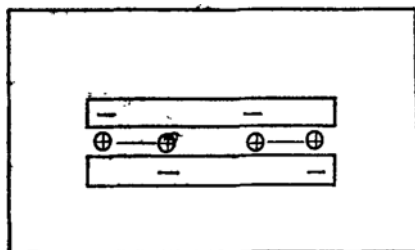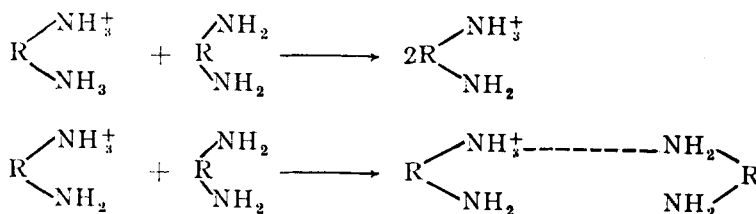
FIGURE 12.

upon acid or Na-montmorillonites and are characterized by the perpendicular orientation of the aliphatic chain and by the occurrence of an $-NH_2$ deformation band. In acid clay the transformation of class I complex into class II occurs gradually and probably through the following steps:

$$R\begin{array}{c} {\nearrow}NH_3^+ \\ {\searrow}NH_3 \end{array} + R\begin{array}{c} {\nearrow}NH_2 \\ {\searrow}NH_2 \end{array} \longrightarrow 2R\begin{array}{c} {\nearrow}NH_3^+ \\ {\searrow}NH_2 \end{array}$$

$$R\begin{array}{c} {\nearrow}NH_3^+ \\ {\searrow}NH_2 \end{array} + R\begin{array}{c} {\nearrow}NH_2 \\ {\searrow}NH_2 \end{array} \longrightarrow R\begin{array}{c} {\nearrow}NH_3^+ --------NH_2 \\ {\searrow}NH_2 \qquad NH_2 \end{array}R$$

The fact that no trace of $-NH_3^+$ is found in the infrared spectra of these complexes when more than 100 millimoles/100 g are adsorbed may be understood by assuming a proton delocalization process, the life-time of $-NH_3^+$ being shorter than the time involved in the deformation frequency.

The formation of class II complexes from Na–clay and diamines is due to the usual coordination process.

When phenomena involved in amines and ammonia adsorption are compared, it appears that they are basically similar as far as conversion into ammonium is concerned but that they differ by the coordination complex formation. Only bidentate ligands seem able to build such coordination bond with adsorbed Na^+ and Ca^{++}.

Calorimetry provides a way for distinguishing between chemical and physical adsorption of ammonia (Mortland, Fripiat, Chaussidon and Uytterhoeven, 1963). Physical adsorption results in an enthalpy change of 13 kcal coming from the reaction $NH_3(g) \longrightarrow NH_3$ (ads) while conversion of gaseous ammonia into hydrated ammonium ions produces a heat effect of 33 kcal. The heat effect rising from the ammination of exchangeable Ca^{++} would be of the order of magnitude of 25 kcal.

Direct calorimetric measurements were performed in order to make a

choice between these various possibilities. Ammonia adsorption isotherms apparently belong either to Brunauer type II or IV but the relative pressures applied here are beyond the application range of the B.E.T. theory. The extrapolation to zero pressure of the straight line portion of the isotherms gives the intercepts (n_0) contained in Table 9. When 13 Å² is taken as the cross-sectional area for liquid NH_3, the surface corresponding to the highest n_0 value (in Ca-montmorillonite) amount to 17 per cent only of the whole specific surface. For H-montmorillonite pretreated under vacuum at 44°C, n_0 approximates fairly well to the C.E.C. (95 meq/100 g).

TABLE 9.—AMMONIA ADSORPTION ISOTHERMS AT 40°C. INTERCEPTS (n_0)
VALUES (PER 100 g SAMPLE)

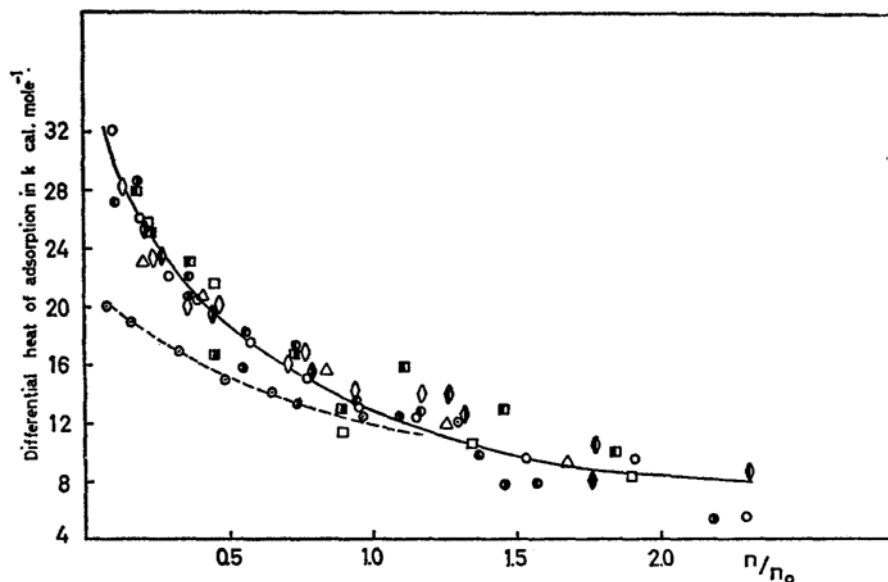| Outgassing temperature before NH_3 adsorption	H-mont.	Ca-mont.	Na-mont.	Ca-verm.
44	95	164	44	72
80	72	70	42	—
150	46	50	30	—
200	39	—	—	—

FIGURE 13.—Calorimetric differential heat of adsorption in kcal vs. n/n_0 H-montmorillonite outgassed at 44°, O; 80°, ◇; 150°, ▫; 200°, △. Ca-montmorillonite outgassed at 44°, O; 80°, ◆; 150°, ▣. Na-montmorillonite outgassed at 44°, ◑; 80°, ◆; 150°, ▣. Ca-vermiculite outgassed at 47°, ⊙.

The ratio n/n_0 has been used as coverage parameter: this choice is justified *a posteriori* by the following considerations.

If the calorimetric differential heats of adsorption are plotted against the n/n_0 ratios the experimental points for montmorillonite samples fit one single function, as represented by Fig. 13. This indicates that, regardless of the cation and the pretreatment, the same thermodynamic processes are involved for the three kinds of samples studied here and that these samples differ only by their sorption capacity. The reason why results for Ca-vermiculite are definitely lower must apparently be found in a greater energy consumption by a diffusion mechanism which, mainly due to the coarser particles and to a lack of expansion in the presence of NH_3, is more important than in montmorillonite.

The comparison of experimental data and theoretical values given above strongly suggests that chemisorption of NH_3 as ammonium occurs for $n/n_0 < 1$. If residual water were not predissociated, the formation of NH_4^+ in base saturated montmorillonite would take up 13.5 kcal, which should be subtracted from the 33 kcal calculated from the transformation NH_3 (g) $\longrightarrow NH_4^+$ (hydr.), thus lowering the net enthalpy change to 19.5 kcal. Results given by Fig. 13 show that the initial differential heat of chemisorption is obviously higher than 30 kcal and support the hyposthesis about the high degree of dissociation of residual water.

The question which arises now concerns the generalization of this dissociation process to amorphous alumino-silicates such as cracking catalysts or to other crystalline species such as molecular sieves. Results reported by Eischens and Pliskin (1958) give evidence' that ammonia is preferentially chemisorbed on Lewis type sites present in cracking catalysts dehydrated at higher temperature ($\simeq 500°C$) whereas a few molecules are converted to NH_4^+ on the Brönsted type of acid sites.

Data reported in Table 3 suggest however that no superficial water molecules subsist under these conditions. On the other hand, even at low temperatures, exchangeable protons are gradually replaced by aluminum extracted by a spontaneous "autolysis process". It might thus be concluded that the existence of protons acting as exchangeable cations or produced by the dissociation of water molecules, although proved at low or "moderate" temperatures, is questionable at higher temperatures.

ACID CHARACTER OF THOROUGHLY DEHYDRATED SURFACES

Heat treatment and evacuation under vacuum successively remove physically adsorbed water and what has been called here "residual water" leaving finally thoroughly dehydrated surfaces. Heating to still higher temperatures induces dehydroxylation. Removal of both "residual water" and "constitution water" often overlaps: this was proved for montmoril-

lonite (Mering, 1947; Fripiat, Chaussidon and Touillaux, 1960) and cracking catalyst (Fig. 2 and Table 3). For silica gels these phenomena are more distinct.

On dehydrated alumino-silicate surfaces it is generally accepted that the only possible acid sites are of the Lewis type. At high temperatures the constitution water contents may be decreased to a limit below which there are not enough hydroxyls to allow the six-fold coordination of aluminum. This idea is supported by the dehydroxylation study of kaolinite but cannot be necessarily extrapolated to other crystalline species. In kaolinite all the aluminum cations are embedded in octahedral layers. Transformation into metakaolinite upon dehydroxylation results into a rather poorly known structure in which aluminum is four-fold co-ordinated (Tscheischwili, Bussem and Weil, 1939; Brindley and Nakahira, 1958 and 1959). Recently this has been directly proved by the X-ray fluorescence technique reported above (Gastuche, Toussaint, Fripiat, Touillaux and Van Meersche, 1963). Figure 14 shows the linear correlation between the Al^{IV}/Al^{VI} ratio and the extent of dehydroxylation.
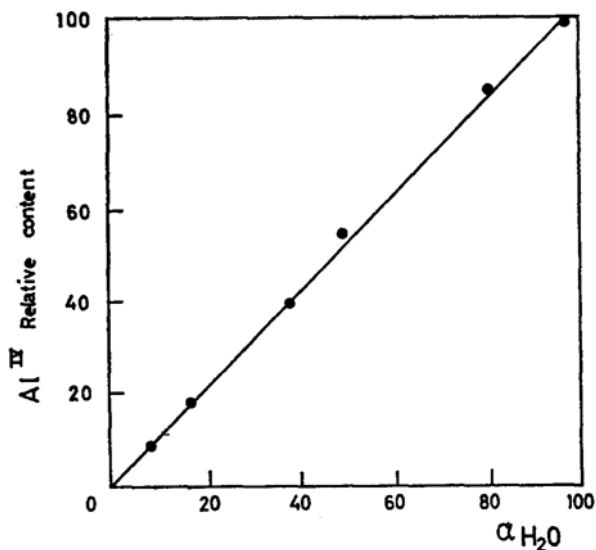

FIGURE 14.—Change in Al coordination with respect to the dehydroxy-lation extent, α H$_2$O, in kaolinite.

The temperature above which such a transformation occurs is of course structure dependent. In kaolinite, under vacuum, it is quite rapidly realized by heating at 450°C. In amorphous but porous gels, it probably occurs under comparable conditions. Here the charge of tetrahedral

alumina is not balanced by a proton but by a hydroxyl deficiency as shown in the following schematic diagram.
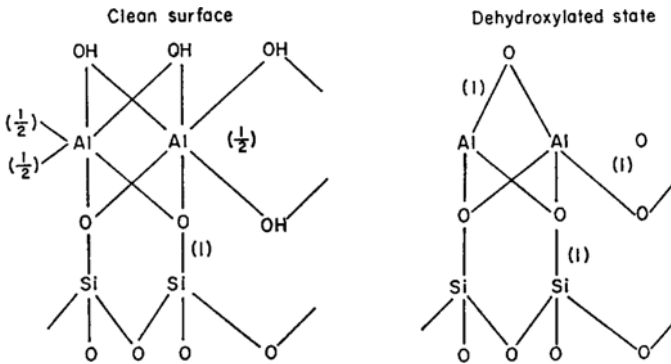
To what extent the sketched tetrahedral alumina might be considered as a Lewis site is not clear.

Usually, a structure like $-O-Al-O$ is supposed to provide such a
$$\underset{\displaystyle O}{\overset{\displaystyle}{|}}$$
site, but it has never been observed in natural nor metamorphic silicates so its existence is highly doubtful other than as a transition state.

However, as Pauling (1945) has noted, tetrahedra sharing edges bring their cations at their centers to a distance from each other of 0.58 times that obtained when they share corners only. Dehydroxylated kaolinite is known to be in a metastable state: the positive Coulomb term arising from cation–cation repulsion causes a large decrease in crystal stability and produces powerful stresses in the structure. The effect of edge sharing is less for octahedra, the corresponding distances factor from sharing edges in place of corners being 0.71. For clays and hydroxides such as gibbsite and brucite, octahedra structures sharing edges as shown are the currently accepted state.

Between the states characterized by the "clean" dehydrated surface or the thorough bulk dehydroxylation, an intermediate state exists in which constitution protons are probably able to move from oxygen to oxygen in the whole or in a part of the lattice structure, including of course the surface. It has been previously shown that constitution hydroxyls of montmorillonite react with ND_3 above 200°C (Mortland, Fripiat, Chaussidon and Uytterhoeven, 1963): infrared and conductometric measurements on heated kaolinite demonstrate this phenomenon even more clearly (Fripiat and Toussaint, 1963).

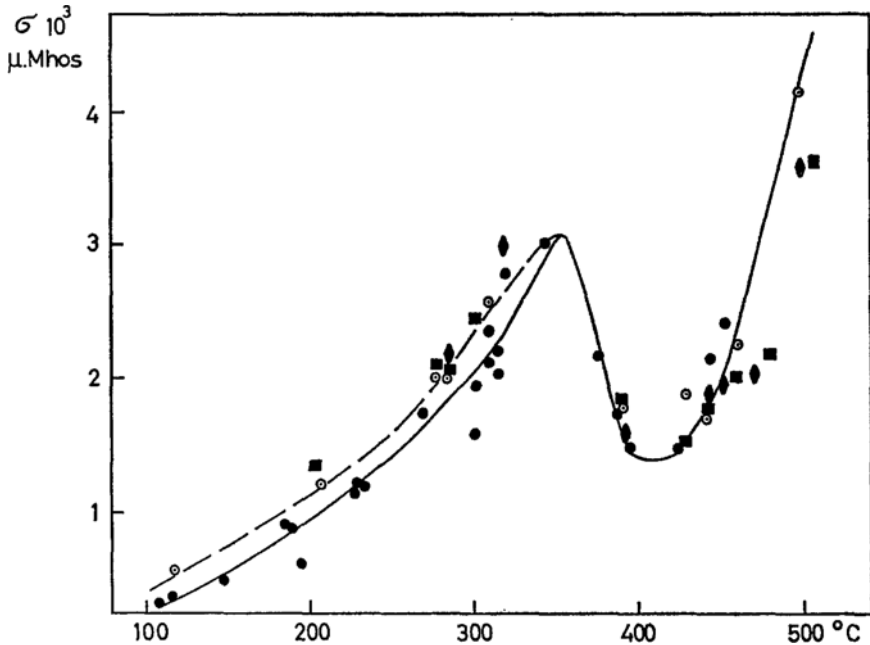Three main features appear when conductivity σ of kaolinite is plotted

FIGURE 15.—Conductivity σ versus temperature of kaolinite plugs: $P_{H_2O} = 10^{-5}$ mm, 0 ; $P_{H_2O} = 0.7$ mm, ●; $P_{H_2O} = 4.8$ mm, ■; $P_{H_2O} = 10.7$ mm, ◆.

against the plug temperature: a rather slow increase between 100° and 360° is followed by a decrease extending from 360° to 420°. A very sharp increase is observed beyond this limit. The flexion preceding is shown in Fig. 15. The sharp rise in activation energies of 4 kcal and 18 kcal are obtained, respectively, from the linear variations of log σ against T^{-1} in the ranges from 100° to 360° and from 420° to 490°. Between 360° and 420° the conductivity decreases with the removal of constitution hydroxyls. This suggests that charge carriers are structural protons and that the conductivity increase occurring between 110° and 360° originates from their increasing mobility.

Moreover the activation energy of 4 kcal is of the expected order of magnitude for the mobility of a hydrogen ion in an environment of close-packed oxygens. For instance the activation energy for the breaking of one hydrogen bond in ice amounts to 5.2 kcal according to Murphy (1951), whereas in water the proton transfer $H_3O^+ \longrightarrow H_2O$ requires 3.9 kcal (Conway Bockriss and Linton, 1956).

The suggested proton delocalization process is also supported by a satisfactory agreement between experimental and theoretical entropy

values obtained for the transmission upon the free oxygen orbitals of the octahedral unit cell (Fripiat and Toussaint, 1963).

On the other hand, if progressive proton delocalization occurs below 360°, the OH and OD stretching bands, located respectively in the 2.7 and 3.7μ regions must change accordingly. This is actually observed for increasing temperature.

Four components are present in the OD-kaolinite stretching band where spectral resolution is the highest and only three in the OH band, i.e., LF, MF$_1$ and HF components. When the temperature is rising their frequencies shift closer to each other, as shown by Fig. 16, but it is probably more than a curious coincidence that above 360°, the frequency shifts no longer appear.
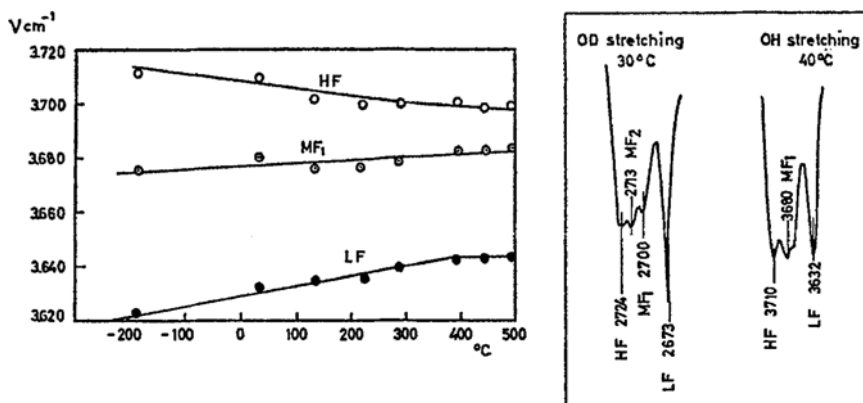

FIGURE 16.—Frequency shift of the HF (O), MF (◯) and LF (●) components of the OH band against temperature.

Thus at 360°, kaolinite may be considered as being in a "predehydroxylation" state characterized by delocalization of the constitution protons.

Without excessively generalizing these findings it seems reasonable to take into consideration this intermediate state in order to explain the catalytic properties of thoroughly dehydrated but not completely dehydroxylated amorphous alumino-silicates.

Another source of acidity on thoroughly outgassed surfaces should be residual silanol groups since even at temperatures as high as 700°C, silica gels keep measurable hydroxyl contents.

Titration in non-aqueous solvents of silica gels shows that silanol groups are characterized by pK values of about 8–9 (Fripiat, Van Compernolle and Servais, 1960). Ionization of silanol groups might be expected with strong bases only. In alumino-silicates however, OH attached to silicon might be "activated" as suggested in the discussion of hydroxyl classifica-

tion, if it belongs to a silicon tetrahedron directly linked to a charge-bearing aluminum tetrahedron.

CONCLUSIONS

The basic feature of silicates is that they develop an oxygen framework either tetrahedrally or octahedrally distributed around polyvalent cations. Some of the oxygen orbitals are used for bonding hydrogen, forming hydroxyl radicals. Some of them are "free" but alternatively occupied by protons from hydroxyls.

According to this representation, the oxygen framework is included in a more or less dense "protonic gas", the mobility of which depends upon structure and temperature. In crystalline species, like kaolinite and montmorillonite, the rate of this delocalization process becomes appreciable at $200°$–$300°C$. In the bulk of the crystal, constitution hydroxyls "belong" to octahedral cells since the strength of the electrostatic oxygen–cation bond is always fractional, while in tetrahedral layer, the electrostatic strength of the bond between oxygens linking adjacent tetrahedra corners is 1. It follows that delocalization probably involves octahedral cells only.

Dehydroxylation originates from the occurrence of two protons on the same oxygen, since at that moment, the oxygen–octahedral cation bond is broken. Dehydroxylation thus begins when delocalization is fast enough to increase above a definite level the probability of such an occurrence. The same principles are valid for surfaces and might explain why aluminum bound hydroxyls are thermally less stable than silanols and consequently why hydroxylic surfaces of alumino-silicates are thermally less stable than those of silica gels.

The main characteristic of aluminum is to be included either in octahedral or in tetrahedral cells whereas silicon is always four-fold coordinated with respect to oxygen. Aluminum tetrahedra are stable in so far as they are embedded in the rigid silicon tetrahedral network and as the charges arising from the Si–Al isomorphous substitutions are balanced by metallic cations other than hydroniums. Metallic cations may be exchanged in solution by H_3O^+, but the silicate is then attacked by its own acidity and $Al(H_2O)_6^{3+}$, produced by "autolysis", spontaneously replaces H_3O^+. This may be interpreted by a peculiar transformation $Al^{IV} \longrightarrow Al^{VI}$ restricted to the surface phase. This transformation involves water molecules thus ruling out any possibility for aluminum to be actually bound to the lattice. For this reason $Al(H_2O)_6^{3+}$ becomes exchangeable.

The stability of Al^{VI} in acid conditions must in some way be related to stabilization by resonance energy resulting from the delocalization process reported above.

In dehydroxylated alumino-silicates, indirect evidence suggests the

existence of Lewis type sites. Four-fold coordinated aluminum is in some way related to such sites. The stress arising in structures by sharing tetrahedral edges may be at the origin of the catalytic activity.

In hydrated samples the surface electrical field polarizes neighboring water molecules in such a way that their degree of ionization becomes much higher than usual. Resulting protons are able to react with ammonia and amines to form ammonium or alkylammonium. Exchangeable protons or "liberated" protons are to some extent delocalized at room temperature since they can move from one hydration water molecule and surface oxygen to another.

Since the pK values for silanols are in the vicinity of 8 to 9, dissociation occurs only at high pH. However, a possibility of being activated exists for silanols neighboring negatively charged aluminum tetradedra; this means that their protons have a higher mobility.

In addition to exchangeable cations, coupling of surface hydroxyls provides privileged water adsorption sites. At low coverage percentages water molecules adsorbed by charged hydroxylic surfaces have lost all their degrees of freedom. They are then strongly restricted to exchangeable cations or to OH adsorption sites. Water molecules, characterized by free rotation and bidimensional translation, are found only in almost complete monolayer.

ACKNOWLEDGMENTS

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