

THE OCTAHEDRAL LAYER

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ABSTRACT

In the first part of this paper the formation processes of pure octahedral hydroxides are investigated. Conditions of synthesis of aluminum, magnesium, iron and mixed Al-Mg, Al-Ca, Al-Fe systems are successively reviewed. In every case crystal growth in deionized medium allows one to figure out genetic conditions.

The second part deals with the conditions required for the development of the octahedral layer in the presence of silica, i.e. the clay mineral synthesis. Experimental conditions remain always as nearly as possible to those observed naturally.

Trioctahedral minerals are rather easily obtained at ordinary temperature and pressure. The evolution of the magnesium-silica system is described. Synthesis of dioctahedral layer lattices, such as those of the kaolin minerals, appears more difficult to perform under the same conditions. Initial organization of the starting materials plays an important role in this case and procedures are described.

Finally, interactions of octahedral and silica layers are studied. The study of infrared spectra in the 9-11 μ region permits such observations. Characteristic changes in the spectral region of Si-O stretching allows one either to follow the octahedral destruction (by acid attack or dehydroxylation) or the octahedral layer formation in kaolinite synthesis.

INTRODUCTION

AGING conditions occurring in the soil differ greatly from the ones generally practised in experimental research. Very dilute solutions renew continuously around soil colloids inducing different types of weathering related to the nature of the percolating solution, its amount and temperature.

"Acid" and "alkaline" notions have not the same meaning for the chemist and for the geologist and pedologist. For these latter, an acid environment will signify pH's ranging approximately between 4 and 6 and alkaline conditions will stand between 7 and 9, as far as pH notions still have a meaning in the colloidal system under consideration.

Thus, genesis of secondary minerals, clays and associated oxides, occurs in a very narrow range of pH, temperature and possibly dilution.

Synthetic products reproducing the chemical composition of secondary minerals seldom evolve towards the forms observed in nature unless some precautions are taken.

One of the main precautions, according to Hénin, Caillère and collaborators (1961), is the use of high dilutions. Under these conditions they have succeeded in synthesizing trioctahedral clay minerals, 2 : 1 layer lattices being favored by "high" pH conditions (8-10), while "low" pH (7-8) induces the formation of 1 : 1 lattices. They assume that the layer lattice organization is induced by the presence of the octahedral hydroxide structure which patterns, even in solution, the bidimensional polymerization of the silicic framework.

The implicit attention of these authors to the solution state has progressively developed into a concept of "preorganization" in the several references cited for Gastuche, Fripiat, De Kimpe and Brindley from 1959 to 1963. Studying the synthesis of kaolin minerals, they noticed that starting materials related to the final products increased the reaction rate so that it may become appreciable at ordinary temperatures and pressures. The knowledge of factors favoring preorganization will be of capital interest for syntheses to succeed.

For Hénin, Caillère and collaborators, factors favoring organization are high dilution and the presence of "potential" octahedral layers.

Gastuche, Fripiat, De Kimpe and Brindley noticed, however, that the stabilization of the octahedral layer is not sufficient to perform kaolin synthesis and insisted on factors favoring bidimensional polymerization of the silicic framework.

Researches have been carried out at Louvain to decide whether the octahedral layer or the silica framework formation is to be considered as the rate limiting progress in clay mineral synthesis.

Fripiat, Léonard and Barake (1963) have recently published a study on the relationship between the texture and structure of silica gel, which may be considered as a first attempt towards a knowledge of the silica framework organization. De Kimpe and Gastuche also have new unpublished results on the same subject, but the attention to silica generally has been less than the great deal of work devoted during these last years to the study of the octahedral hydroxides.

The results obtained being of interest for the study of kaolinite and clay mineral synthesis, the aim of this paper will be to describe the experiments performed in this direction.

DESCRIPTION OF DIFFERENT OCTAHEDRAL HYDROXIDES OBTAINED BY SYNTHESIS

1. *Aluminum Trihydrates*

In order to understand laterite formation under tropical climates, Gastuche and Herbillon (1962) compared the aging of alumina gels precipitated from aluminum chloride by NaOH at different pH's (4.5,

TABLE 1.—INFLUENCE OF THE KIND OF AGING ON THE EVOLUTION OF THE ALUMINA GELS

Kind and period of aging	t°	Gel precipitated at pH 8			Gel precipitated at pH 6.5			Gel precipitated at pH 4.5		
		S ₀ m ² /g	X.R.	%H ₂ O	S ₀ m ² /g	X.R.	% H ₂ O	S ₀ m ² /g	X.R.	% H ₂ O
(a) Aging in the mother solution	1 day	193	Ps. Bh.	24.0	80	Am.	29.9	8	Am.	45.5
	1 month	184	Ps. Bh.	21.1	12	Am.	32.0	6	Am.	42.2
	2 months	111	Ps. Bh.	21.3	34	Am.	33.9	6	Am.	44.2
(b) Aging in dialyzed medium	1 month	71.6	Gb. Ba.	34.2	—	Ps. Bh. + Ba.	33.0	53.0	Gb.	36.1

Legend: X.R.: X-ray diffraction character
 Ps. Bh.: pseudo-boehmite gel (Calvet *et al.*, 1953)
 Gb.: gibbsite
 Ba.: bayerite
 Am.: amorphous

Herbillon and Gastuche (1963) investigated also the influence of kaolinite surfaces, seeding the alumina gels by this clay, and made the following statements:

(a) *Aging in the mother solution.*—Preferential orientation is noticed depending on the pH. At pH 4.5, gel and kaolinite phases separate when centrifuged. At pH 6.5 the amorphous gel precipitates outside the kaolinite platelets. At pH 8 the gels particles orient upon the 001 planes and gather in "somatoids". After one month crystallization to bayerite begins. Hydration, surface area and crystallizations observed in these mixed systems are given in Fig. 1.

(b) *Aging in dialyzed medium.*—Whatever the initial pH of precipitation, dialysis induces very rapidly trihydrate crystallization. The situation is then entirely comparable to that observed for the pure aluminic system.

2. Iron (Fe^{3+}) Hydroxides

Mackenzie (1957) observes that a ferric hydroxide precipitated by NH_4OH at pH 10 crystallizes to goethite: when precipitated at pH 5 it remains mainly amorphous, even after 155 days.

Schellman (1959) emphasized the role of ionic impurities in the crystallizations obtained. Goethite forms at high pH (11–12), while hematite is favored by a low pH environment. According to this author, both minerals appear also in neutral solution but anionic impurities, such as CO_3^{-2} or SO_4^{-2} , induce goethite formation, while cationic ones, as Mg^{+2} or Ca^{+2} , provoke the evolution towards hematite. Ions such as K^+ , Na^+ , Ba^{+2} , Cl^- , NO_3^- do not influence noticeably these processes.

Gastuche, Bruggenwert and Mortland (1964) observed that, in a dialyzed medium, hematite crystallizes rapidly from ferric gels prepared at low pH (4.5), producing very dark, hard "iron concretions" that separate from a sol-phase. Under the same conditions but above pH 8, goethite begins to appear together with hematite, its yield increasing with rising initial pH. These high pH gels prepared with NaOH or KOH always remain flocculated.

3. Mixed Al-Fe Systems

Gastuche, Bruggenwert and Mortland (1963) also studied the evolution of mixed Al-Fe systems in a dialyzed medium.

(a) Mixed gels coprecipitated at low pH and high in aluminum separate into two phases: one, light-brown, almost white and aluminum-rich, passes through a sol-phase and crystallizes to gibbsite; the other one, dark-red, remains flocculated at the bottom of the bag. The only mineral present in this last phase is a poorly crystallized gibbsite with apparently distorted parameters (Fig. 2). Bayerite with distorted parameters appears for increasing iron content and, in medium to high ferric systems, amorphous

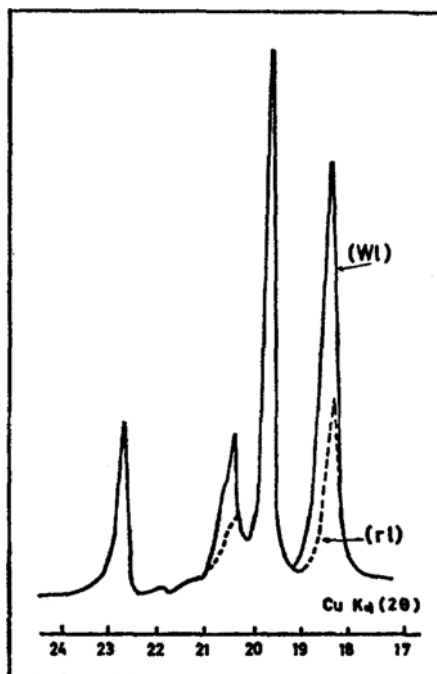


FIGURE 2.—X-ray diagrams of the white layer (w.l.) and the red layer (r.l.) obtained after 19 days of aging in dialyzed medium at 20°. The initial Al/Al + Fe molar ratios are 95 per cent. The red layer is poorly crystallized and some evidence of distortion appears in gibbsite parameters. [4.87 Å and 4.35 Å].

phases only are found. At the end of the concentration range, hematite crystallizes.

(b) Gels precipitated at high pH and dialyzed present one phase only. Goethite forms in pure ferric systems, but as soon as aluminum is present hematite is the only crystalline species, and it is characterized by distorted parameters. For high aluminum contents a mixture of gibbsite, bayerite and nordstrandite appear (Fig. 3). The relative yield depends not only on the base used for precipitation but also on the cation present in the dialysis solution, as illustrated in Table 2.

In these mixed ferric and aluminic systems hematite and bayerite are the species able to stand the highest amount of isomorphous substitution. The distortion in hematite and bayerite parameters arising from isomorphous substitutions are clearly visible on the X-ray patterns as illustrated in Table 3. Such a change, however, is more questionable for gibbsite. Electron micrographs show a continuous series of distorted crystals with

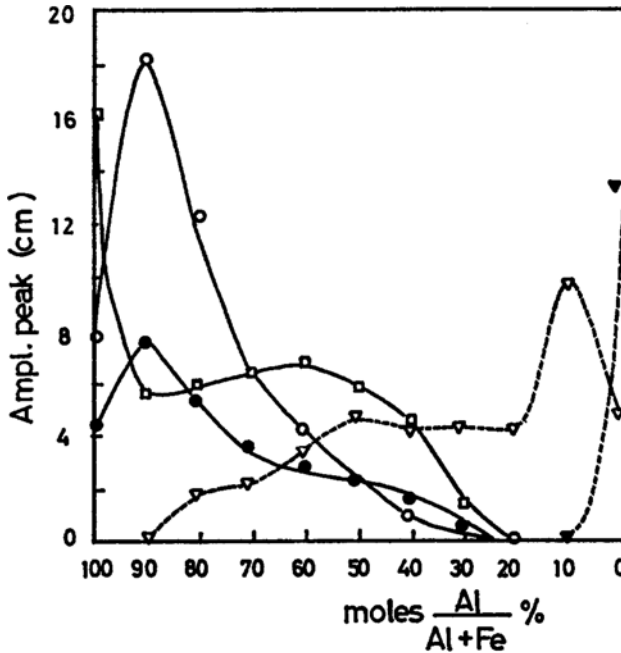


FIGURE 3.—“Phase diagram” obtained for samples prepared from potassium aluminate and ferric chloride and precipitated at pH 10. The gels were dialyzed during one month at 60° with a KOH solution at pH 10 in order to maintain constant pH.

In abscissa is the initial molar content in Al/Al + Fe and in ordinate is the measured peak height amplitude of the X-ray reflection which was considered as characteristic for each given mineral. Chosen peaks were the following: ● gibbsite 4.85 Å, ○ nordstrandite 4.785 Å, □ bayerite 4.71 Å, ▽ hematite 2.514 Å, ▼ goethite 4.18 Å.

TABLE 2.—CRYSTALLIZATION OBSERVED FOR 0.5 MOLES Al/Al + Fe (INITIAL RATIO) PRECIPITATED FROM CHLORIDES WITH NaOH AT pH 10 AFTER 30 DAYS DIALYSIS

Dialysis solution	Crystallization observed (peak amplitude in cm)				
	Gb	N	Ba	He	Gt
KOH at pH 10	—	2.0	—	0.5	—
NaOH at pH 10	—	8.0	5.8	5.5	—

Legend, Gb: gibbsite, N: nordstrandite, Ba: bayerite, He: hematite, Gt: goethite.

TABLE 3.—PARAMETERS MEASURED IN THE EXPERIMENT CARRIED OUT WITH POTASSIUM ALUMINATE AND FERRIC CHLORIDE ILLUSTRATED IN FIG. 3

			4.85	4.785	4.71	
Gibbsite						
Nordstrandite						
Bayerite						
Goethite		4.98				
Hematite						3.67
Moles	Al	1.00	4.859	4.795	4.72	
	Al+Fe	0.90	4.845	4.805	4.725	
		0.80	4.859	4.805	4.725	
		0.70	4.859	4.805	4.715	3.643
		0.60	4.859	4.805	4.725	3.667
		0.50	4.858	4.805	4.720	3.676
					4.742	3.669
	0.40		4.859		4.72	3.661
					4.725	3.671
	0.30				4.762	3.667
	0.20					3.656
						3.671
	0.10					3.698
	0.00	4.986				3.687

TABLE 4.—CRYSTALLINE SPECIES PRESENT, EXCEPT KAOLINITE, IN MIXED Al-Fe GELS PRECIPITATED UPON KAOLINITE SURFACE AND AGED ONE MONTH IN DIALYZED MEDIUM AT 60°

Initial content in moles Al	moles Fe	Precipitation with NH ₄ OH at pH 9	Precipitation with NaOH at pH 10	Precipitation with NaOH at pH 4.5
moles Al + Fe	moles Fe + Al			
100	0	Gb	Ba	Gb
80	20	Gb	Ba	Gb
60	40	Gb	Ba + He	Gb, Gt, tr (He*) (w.l.)
40	60	Gb, He, Ba	Ba	Gb, tr, Gt (r.l.)
20	80	He, Ba	Gb, He, Gt	Am
0	100	He, Gt	Gt + He	tr, Gb, tr, Gt, He

Legend: Gb, gibbsite; Ba, bayerite; He, hematite; Gt, goethite; tr, trace; w.l., white layer; r.l., red layer.

increasing Fe amounts (Plate 3). Some electron diffraction data observed for these crystals also indicate the isomorphous substitution.

Results concerning the influence of kaolinite surfaces upon the parallel evolution of Al-Fe systems, the composition of which are given in Table 4, are still unpublished.

An interesting observation is that in the presence of kaolinite, goethite appears even when aluminum is introduced in the system and even at low pH (Plates 1 and 2).

4. Mixed Al-Mg Systems

Feitchecht (1942), Feitchecht and Gerber (1942) have shown that a large number of different layer lattice structures result from the combination of divalent and trivalent cations with similar ionic radii. They describe them as "double hydroxides" while French authors (i.e. J. Longuet-Escard (1951)) call similar substances "aluminates". Mortland and Gastuche (1962) prepare the mixed Al-Mg hydroxides from the corresponding chlorides aged in a dialyzed medium, achieving in this way a much better crystallization and a higher purity. They find two double hydroxides.

The first one is characterized by the higher magnesium content and has parameters slightly larger than the second species, richer in aluminum.

Their structure, not yet completely established, has been studied recently

TABLE 5.—POWDER DIAGRAM AND CHEMICAL ANALYSIS OF THE TWO AL-MG DOUBLE HYDROXIDES

I		II		I		II	
$d(\text{\AA})$	<i>I</i>	$d(\text{\AA})$	<i>I</i>				
7.95	v. v. s.	7.63	v. s.	H ₂ O	32.36	34.80	
3.96	v. s.	3.80	s.	CO ₂	9.05	7.36	
2.61	s.	2.58	m. s.	Al ₂ O ₃	15.08	18.72	
—		2.525	w.	MgO	43.49	39.11	
		2.34	m. w.				
2.03	m. w.	1.983	w.				
—		1.890	v. v. w.				
1.53	m. s.	1.519	m. s.				
1.502	m. s.	1.489	m. s.				
1.426	w.	1.409	w.				
—		1.305	w. halo				
1.317	v. w. halo	1.263	w. halo				
1.280	v. w. halo	—					
1.0017	v. v. w.	0.9948	v. v. w. halo				
0.984	v. v. w.	0.9738	v. v. w. halo				

by Gastuche, Mortland and Brown but is not yet published. Substitution of aluminum for magnesium induces positive charges which are compensated by anions, by chlorides in Feitchnecht's samples, aged in the mother solution, and by carbonates in the dialyzed Mortland and Gastuche's samples (see Table 5 and Plate 4).

The last ones are very definite compounds. Excess of magnesium leads to crystallization into brucite, and high aluminum samples contain bayerite.

Al-Ca, Fe-Mg and Fe-Ca systems must also lead to double hydroxide systems. Among them only the Al-Ca compound has yet been reproduced in the laboratory (Gastuche and De Kimpe, still unpublished) and resembles by its X-ray patterns and chemical composition the Al-Mg hydroxide.

Hydrotalcite (Fron del, 1941) and hydrocalumnite (Tilley, Megaw and Hey, 1934) are the natural homologues of these synthetic compounds.

MECHANISM OF THE OCTAHEDRAL LAYER FORMATION

An attempt has been made to follow every step of the evolution between the fresh amorphous hydroxide and the crystalline phases. This has been fulfilled only partially. Crystallization processes are not easily reproducible at the present time, being more an art than an expression of rigorous scientific backgrounds. Consequently, experimental procedures providing useful information are still scarce. The following measurements were carried out:

(i) *On the suspension*, pH, conductivity, tonometry, evaluation of the particles size by light scattering, measurement of the ξ potential by micro-electrophoresis.

(ii) *On the dried samples*, electron microscopy, electron diffraction and X-ray diffraction, D.T.A. and infrared spectroscopy, B.E.T. surface area determinations, measurement of Al coordination by X-ray fluorescence (White, McKinsty and Bates, 1958; De Kimpe, Gastuche and Brindley, 1961).

1. *Physical Evolution of Pure Ferric and Aluminic Samples*

Special attention has been given to gels precipitated at low pH, which do not crystallize unless a deionization process is applied. As far as the mechanisms are concerned, aluminum gels were studied by Gastuche and Herbillon (1963), while Al, Fe and mixed Al-Fe gels were studied by Gastuche and De Flandre (1963).

When fresh pure ferric and aluminum hydroxides are dialyzed, macroscopic changes occur in the suspension with respect to the time. When

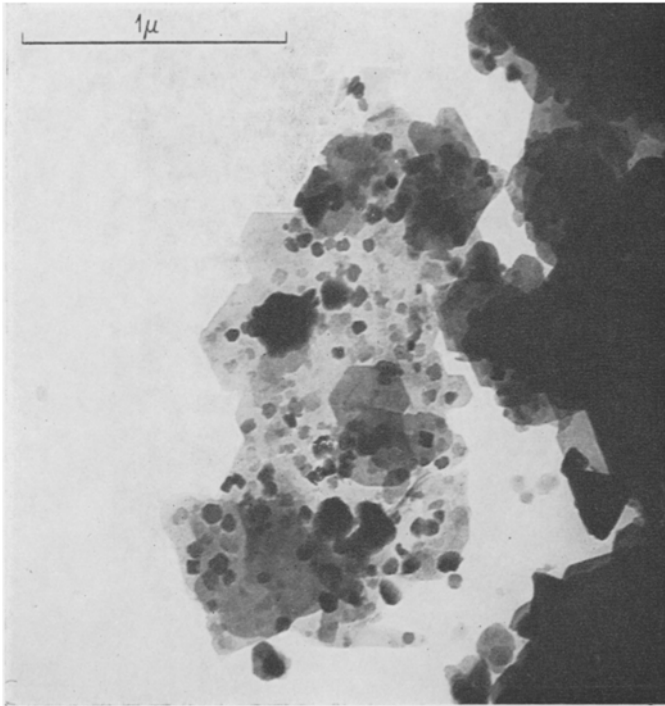


PLATE 1.—Zettlitz kaolin with oriented gibbsite crystals obtained from an experiment performed by aging a pure aluminic gel on kaolinite.

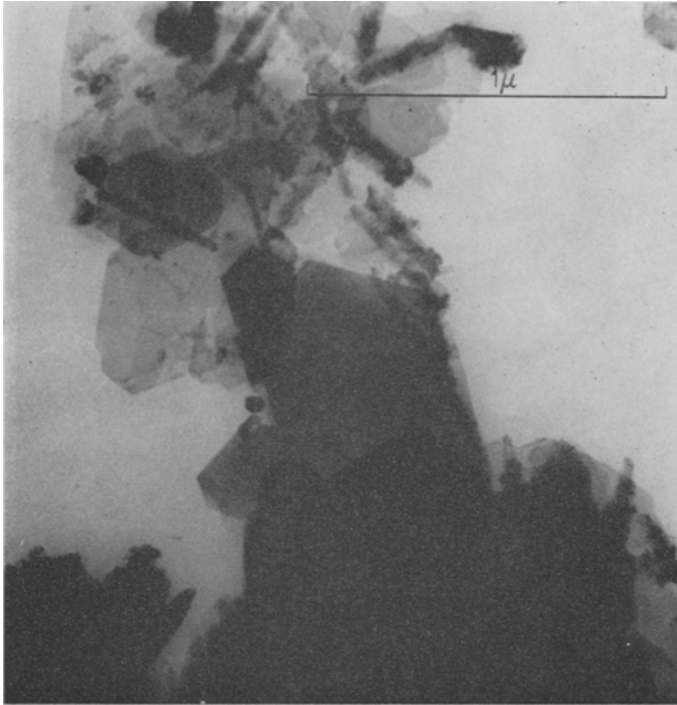


PLATE 2.—Zettlitz kaolin with goethite crystals from an experiment performed by aging in a dialyzed medium a mixed Al-Fe gel precipitated at pH 10 with relative molar Al/Al + Fe ratio equal to 0.2.

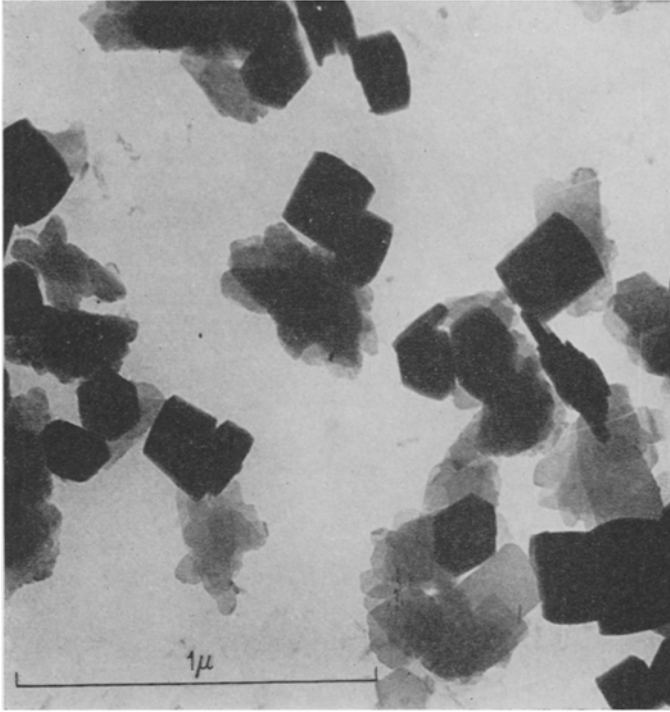


PLATE 3.—Gibbsite with an initial molar Al/Al + Fe ratio of 0.95 prepared by precipitating Al and Fe chlorites at pH 4.5 and aged during one month in a dialyzed medium.



PLATE 4.—Mg-Al double hydroxide, form 1, aluminum-rich.

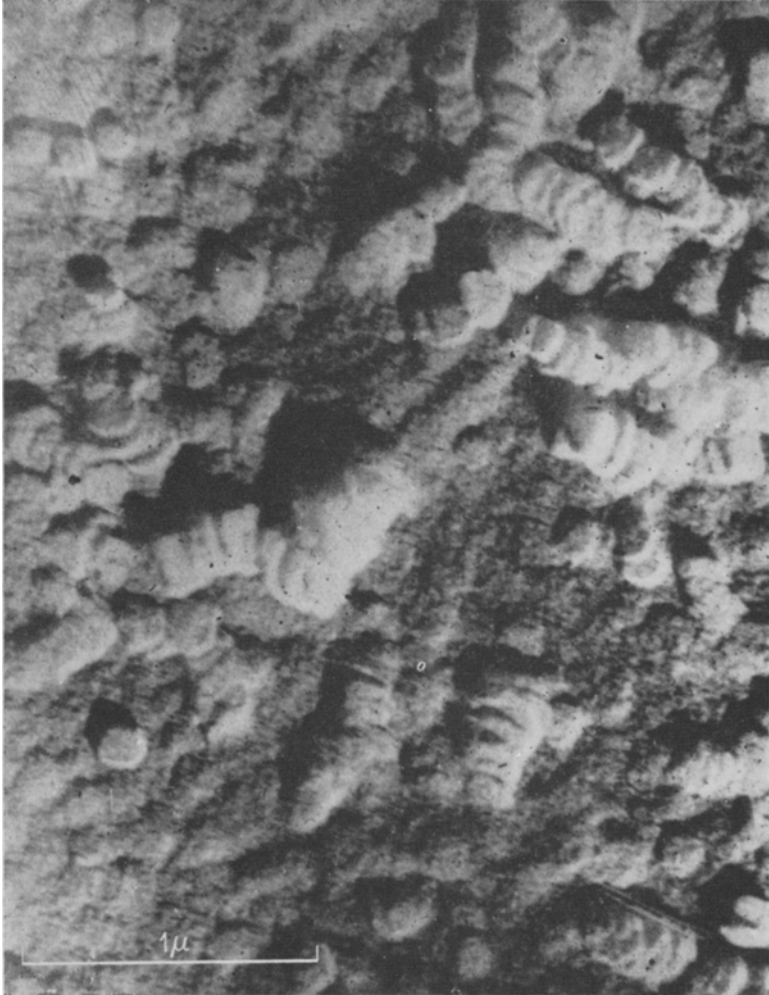


PLATE 5.—Shadow casting improves the resolution in the third dimension and shows the piling-up of somatoids in the course of gibbsite synthesis.

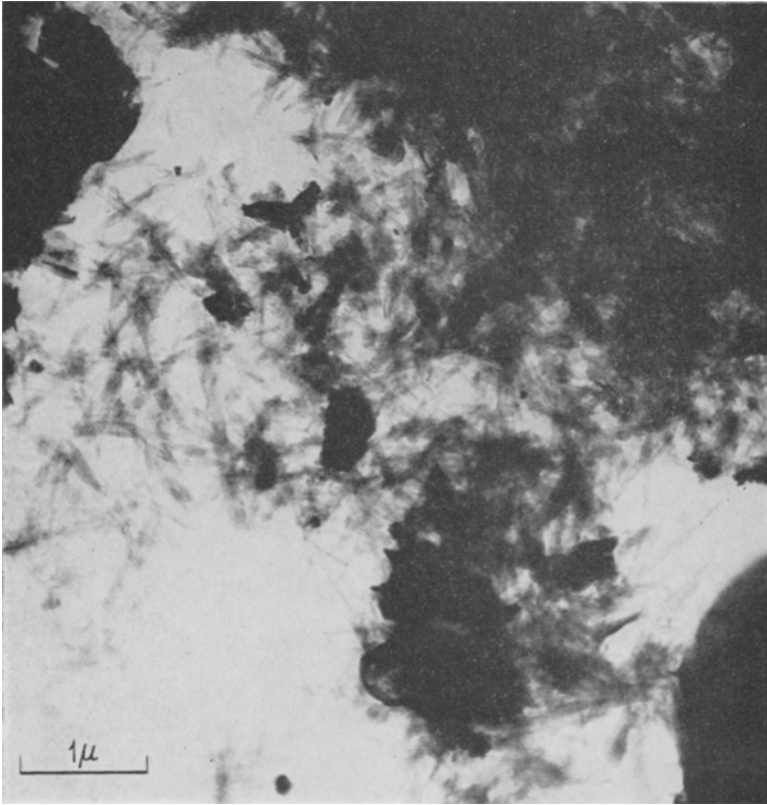


PLATE 6.—Lath-like synthetic kaolin.

TABLE 6.—EVOLUTION OF Al GEL PRECIPITATED AT pH 4.5 — 4.8 AND DIALYZED

	Specific surface m ² /g	%H ₂ O	%Al ^{IV}	Electron microscopy	E.D.	X-ray	Infrared	
							9-13 region	3 (OH) valence vibration
Fresh gel	5-8	43-50	60-70	very agglomerated gel	nothing	nothing	band at 1004 cm ⁻¹	poor definition
Intermediate stages: depolymerization	100-200	20-30	decreases	depolymerization	nothing	nothing	band at 1004 cm ⁻¹	poor definition
Pregibbsitic stage	very high surface 200-500	33-35	0	spherical particles of about 50 Å diameter	nothing	intense reflection at 6.5 Å	band at 1004 cm ⁻¹ disappears, torsion band	better definition
Intermediate stage: somatoids	decrease in surface area	35	0	bidimensional agglomeration of spherical particles (somatoids) (Plate 5)	Gb (powder diagram)	Gb (powder diagram) Gb begins	appearance of Al-O vibration at 800 cm ⁻¹	
Crystalline state	surface determined by the size of the crystallites	35	0	piling-up of the somatoids along 001 direction	Gb (monocrystal)	Gb (perfect)	typical gibbsite diagram	typical gibbsite diagram

dialysis is run below pH 6.5 this evolution may be summarized into three main steps as follows:

	Al ³⁺ + HYDROXIDE (precipitated from AlCl ₃)	Fe ³⁺ + HYDROXIDE (precipitated from FeCl ₃)
(i) Fresh gel	white and voluminous	dark-brown.
(ii) Sol-phase	colorless translucent "pregibbsitic stage"	brown translucent.
(iii) Crystallization period	"milky" flocculate containing crystalline trihydrates	dark-brown "concretions" separate from the sol-phase, glossy and hard when dried.

The depolymerization is followed by an agglomeration of the micelles in two-dimensional platelets ("somatoids") the size and shape of which pattern the future hexagonal gibbsite crystals. The electron diffraction powder diagram of the *hko* gibbsite planes is already observed and the the (002) reflection appears in the X-ray pattern. The depolymerized "pregibbsitic" gel is amorphous from the viewpoint of electron and X-ray diffraction. The X-ray diagram shows a unique reflection towards 6.5 Å. The formation of gibbsite progresses further on by piling-up somatoids along the 001 direction, while infrared and X-ray patterns become progressively typical (see Plate 5 and Table 6) until beautiful hexagonal platelets are obtained. Their size increases with increasing aging temperature. Table 7 compares the diameters of average crystals measured (i) by light scattering, (ii) by electron microscopy. The agreement between both sets of measurements is to be expected if the particle size distribution is homogeneous.

Similar features are observed for low pH ferric gels when dialyzed. Iron

TABLE 7.—COMPARISON BETWEEN THE PARTICLE DIAMETER MEASURED EITHER BY LIGHT SCATTERING (L.S.) OR ELECTRON MICROSCOPY (E.M.)

Temp. of aging	Time (days)	Stage	<i>d</i> Å (L.S.)	<i>d</i> Å (E.M.)
43 ± 1°C	4	somatoid	1800	1830
	5	crystal	1800	
	6	crystal	2130	
80 ± 1°C	3	somatoid	1960	3200
	5	crystal	2350	

and aluminum hydroxides freshly precipitated at low pH (4-5) are characterized by a low surface area and high water content. The sol-phase displays high surface area while crystallization coincides with noticeable decrease of this parameter. Accordingly, water content reaches the level expected for the corresponding crystallized species.

Micro-electrophoresis measurements have shown that both ferric and alumina gels prepared at low pH bear positive electrical charge, the highest ξ potential being observed at the "sol stage" (Fig. 4).

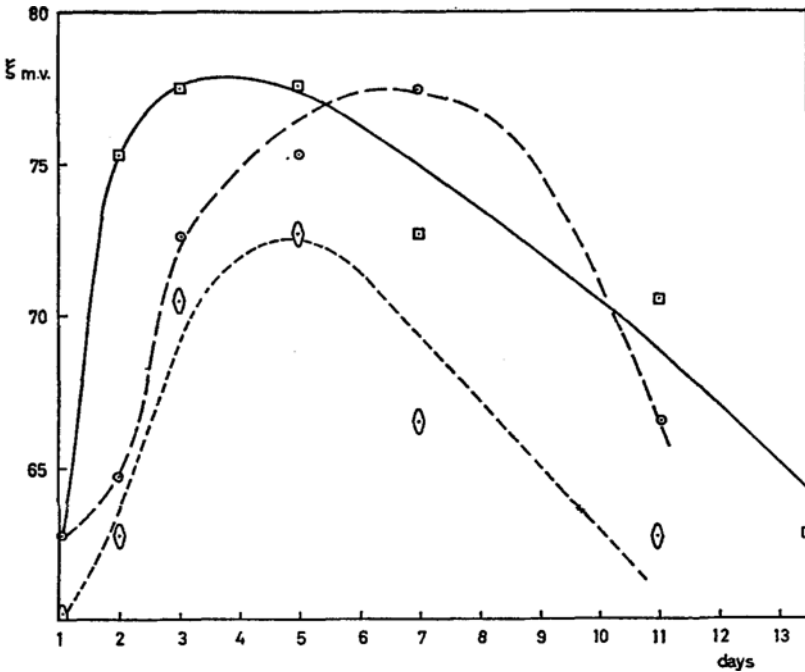


FIGURE 4.—Evolution of the ξ potential for gels precipitated at pH 4.5 and dialyzed at the temperature of 50°C. In abscissa is the time of aging, in ordinate the ξ potential in mV. Highest ξ potential coincides with highest depolymerization. ○, pure ferric gel; □, gel with initially 5 per cent by mole Al/Al + Fe; ◇, gels with initially 95 per cent by mole Al/Al + Fe.

When dialysis processes are applied to either ferric or aluminic hydroxides precipitated at high pH (8-10), the evolution is quite different, since the gels remain flocculated during the whole crystallization period. This prevents the measurement of electrical charge by micro-electrophoresis and clear observation of the morphological changes by electron microscopy.

2. Water Activity Measurements on the Suspensions

The osmotic pressures in the dialysis cellulose bags in which hydroxides evolve towards the crystalline state are apparently variable according to the nature of the species. Under similar conditions of concentration the swelling is more pronounced for aluminic than for ferric samples.

Attempts were made to correlate these observations to the measurements of water thermodynamic potential either by cryoscopy or tonometry. The first method was unsuccessful because of the formation of glassy states without any definite freezing point. Tonometric measurements on the other hand brought interesting information: they were performed with Fripiat and Delfosse's (1963) modified version of Richards and Ogata's tonometer (1958).

This apparatus allows one to obtain the chemical activity a as related to the chemical potential μ according to the relationship

$$\frac{\mu - \mu_0}{RT} = \ln a$$

μ_0 being the chemical potential of the pure water.

The activity is equal to the molar fraction of the water in the suspension, as far as the activity coefficient may be considered as equal to unity, and this condition is approximately fulfilled in the dilute systems under consideration.

Thus, it becomes possible to evaluate the numbers of associate molecules bound in gel particles aging in the suspensions. These may be expressed in terms of molecular weights. Results shown in Table 8 demonstrate that this parameter depends upon the nature of the gels and the precipitation pH values. Data obtained for alumina gels prepared at low pH are uncertain (data between brackets) but it seems that the weight with them is several times higher than that observed for the pure ferric gels. Mixed systems give intermediate results.

The crystallization processes of aluminum trihydrates appear to be strongly pH dependent. The depolymerization state observed at low pH for the aluminic system results probably in clathrating a high number of water molecules, while under similar conditions the ferric particles do not accommodate so much water. These differences are reflected in the kind of crystalline species obtained: gibbsite in the first case, hematite in the second one.

Explanation of these differences could be found either in the polarizing power, which is lower for Fe^{3+} than for Al^{3+} . Any quantitative treatment

TABLE 8.—MOLECULAR WEIGHTS M CALCULATED FROM WATER ACTIVITY DATA FOR HYDROXIDE DIALYZED AT 50°C

Time in days	Pure Fe gel prec. at pH 4.5	Mixed Fe-Al gels $\frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} = 92\%$	Mixed Fe-Al gels $\frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} = 87, 8\%$	Pure Al gel prec. at pH 4.5
	M cryst.	M cryst.	M cryst.	M cryst.
1	3104	3158	6909	19102
2	2904	3158	—	(20152)
3	3064	—	—	(14582)
	1639 (CO ₂) Am			—
4	2804	3538	7712	18102
5	4104	3778	not meas- urable	not meas- urable
7	3864	4438	two phases	cryst. starts
11	(1634)	4038	Gb ₁ Gb ₂ (see Fig. 3)	Gb

Crystallization partially poisoned
for some unknown reason

Constant progress in crystallization.

of the problem would include intricate conditions and seems hardly possible.

3. *pH, Ionic Content and Coordination*

The passage from the fresh gel to the sol state is accompanied by a decrease in pH below the level at the initial stage of the precipitation, and by a subsequent increase to about 5.5. This has been observed during the evolution of aluminum gels, whatever the pH of precipitation, and for ferric gels precipitated at low pH. For ferric gels precipitated at high pH, which evolve to goethite, the pH decrease is monotonic to 5–6.

As already outlined, the depolymerized "sol" stage observed for the low pH evolution is connected with the anion removal adsorbed by the positively charged particles at the early stage of the precipitation. Cationic impurities, probably present in high pH gels, have a weaker effect on the octahedral structure development. They are less polarizable and do not preclude the organization of the OH ligands around the polyvalent cation. Cations are more easily expelled from the micelle so that crystallization may occur even in the mother solution. Under acid conditions, the removal of anions is the rate controlling mechanism, the diffusion process in the gel phase being accelerated by increasing the temperature. For Al gels prepared at pH 4.5 from AlCl_3 , Gastuche and Herbillon have measured an activation energy of $5.5 \text{ kcal/mol}^{-1}$, which is of the order of magnitude expected for a diffusion phenomenon.

Anionic impurities do not act all in the same way and their influence depends on the precise time when they are added.

One must distinguish between: (i) easily extractible, univalent, weakly polarizable anions like Cl^- , NO_3^- and (ii) non- or difficultly extractible anionic impurities, highly charged and very polarizable, such as CO_3^{2-} , which induce the formation of gelatinizing phases, or anions able to bond iron or aluminum, like PO_4^{3-} and SiO_4^{4-} which fix into the system and induce the formation of new compounds, either phosphates or silicates. Study of phosphate fixation by these systems was undertaken by Gastuche, Sokolsky and Fripiat (1963). The anions present at the early stage of the precipitation process strongly influence the coordination number of the metal cation. The percentage of fourfold coordinated aluminum decreases in gels prepared at low pH from AlCl_3 , in accordance with the chloride removal. In dialyzed medium, the Al^{VI} form is obtained very quickly at the "pregibbsitic" stage (see Tables 9 and 6).

The X-ray fluorescence method being not applicable for determining the iron coordination number, it is not certain that the same mechanism may be involved for ferric hydroxides. However, the role played by the anion such as Cl^- becomes more easily understandable from the coordination viewpoint.

TABLE 9.—CHANGE IN AL COORDINANCE IN DRIED GELS

pH	Time of aging in the mother solution	% Al ^{IV}	% H ₂ O	So m ² /g	Crystallization
8	1 day at 20°C	36	24.9	193	Ps. Bh
	1 month at 20°C	20	21.1	184	Ps. Bh
5.5	1 day at 20°C	67	37.3	59.3	Am.
	3 months at 20°C	50	39.5	116.5	Am.
4.5	freshly precip. at 20°C	60	45.5	8	Am.

In an acid medium they preclude the regular distribution of the six OH ligands around the central metal atom and the post-deionization process appears as fundamental in the crystal growth process.

INFLUENCE OF OCTAHEDRAL LAYER IN CLAY-MINERAL SYNTHESIS

As outlined in the introduction, an important role of orientation is attributed to the octahedral layer in the bidimensional development of the silicic framework.

Since it was proved that the aluminum octahedral layer is easily stabilized at low pH, provided anionic impurities are removed, synthesis of kaolin minerals seems at the first sight easy to perform.

Papers by Gastuche and De Kimpe (1959), Gastuche, De Kimpe and Fripiat (1961), De Kimpe, Gastuche and Brindley (1961) (1963), Brindley and De Kimpe (1961) throw some light upon the problem.

They make the following statements:

(i) *Comparison of dioctahedral and trioctahedral 1 : 1 layer lattices.* By hydrolyzing aluminum and magnesium foils in the presence of dilute silica solutions, they observe that under similar conditions a 1 : 1 serpentine mineral forms at pH 7–9 with good X-ray patterns, while only traces of 1 : 1 aluminic phyllites appear at pH 4.5–5, with the bulk evolving as a mixed gel phase.

(ii) The aging of mixed Al–Si gels with an Al–Si 1 : 1 ratio shows that the Al coordination depends on pH: Al^{VI} is stabilized at low pH, even in the presence of chloride, and Al^{IV} appears for high pH gels (above pH 5.5) and increases with increasing pH (see Table 10).

The presence of silica thus changes completely the Al^{IV}–Al^{VI} equilibria observed previously for pure Al gels. At high pH, SiO₄⁴⁻ plays the role of perturbing anions inducing Al^{IV} formation, as proved by infrared spectroscopy.

At low pH, where Al^{VI} is stabilized, kaolinite is obtained, as proved by

TABLE 10.—PERCENTAGE OF Al^{IV} IN MIXED 1 : 1 Al : Si GEL IN FUNCTION OF pH AND AGING PERIOD AT ORDINARY TEMPERATURE

pH	% Al^{VI} in function of time			
	1 week	1 month	2 months	3 months
1.5	94	69	64	82
2	72	59	69	67
4	64	54	72	64
5.5	36	26	51	39
6	36	26	46	44
8	13	0	26	15

electron microscopy and diffraction; but for unknown reasons the yield in crystalline species is always poor.

(iii) Attempts were then made to stabilize the Al^{VI} layer, using already preorganized alumina gels evolving towards gibbsite in a dialyzed medium or crystalline gibbsite itself.

At a given time in the evolution, the dialysis water is replaced by very dilute depolymerized silica solutions. Results of these kind of experiments are condensed in Table 11.

There is no evidence that seeding either with kaolinite or with gibbsite favors the reaction.

Thus, preorganization of the gibbsite layer is not sufficient to induce the complete development of the kaolin layer lattice.

(iv) Gibbsite only fixes silica at $175^{\circ}C$, under water vapor pressure. The synthesis succeeds only at a very low pH (1.5) and a good yield in crystalline phases is found for gibbsite, bayerite, pregibbsitic and other dialyzed gels; no results are obtained for fresh alumina gels or boehmite.

The influence of seeding (muscovite) is positive in this case, where appreciable yield in kaolin is observed up to pH 3.

The kaolin morphology obtained is very variable:

(i) From large "Alcoa" gibbsite crystals a lath-like kaolin is obtained, which may roll into halloysite crystals (Plate 6).

(ii) Small sized gibbsite and dialyzed gels give beautiful hexagonal "classical" kaolinite platelets.

(iii) Half poisoned syntheses give either "allophane" spheres together with halloysite, or other crystalline phases.

The following conclusions may be drawn from this set of syntheses: a "dynamic" Al framework is required to react with silica. It may be attained either by building up an octahedral layer (e.g. dialysis synthesis) or by destroying it (semi-hydrothermal synthesis at $175^{\circ}C$).

Although Al^{VI} coordination is stabilized at low pH and fresh Al gels

TABLE 11.—RESULTS OF AL-SI SYNTHESIS IN DIALYZED MEDIUM

Alumina source	SiO ₂ conc. in dialysis solutions	t°C	X-ray	E.M. + E.D.	Obs.
Gibbsite	40 mg/l.	61	gibbsite	gibbsite	gibbsite
	120 mg/l.	43	gibbsite	gibbsite	does not fix silica
Fresh Al gel prep. with AlCl ₃ .6H ₂ O and NaOH and slightly purified by dialysis	40 mg/l.	61	am. traces of bayerite	—	irregular fixation of silica depending on the flow rate and the temperature
		43		halloysite bayerite kaolinite (b=8.93 Å)	
Pregibbsitic gel	10 mg/l.	61	strong pseudo-boehmite reflections		1-2 per cent of silica fixed

react with silica, synthesis of kaolin mineral is not achieved under these conditions, so that another factor must play a determining role.

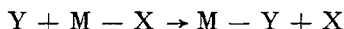
Fripiat and Gastuche (1963) point out the importance of the silica layer preorganization, which is probably mainly influenced by the pH and cationic content of the medium.

Further still unpublished experiments by Gastuche and De Kimpe show that traces of cations influence greatly the polymerization of the silicic framework.

DISCUSSION AND CONCLUSION

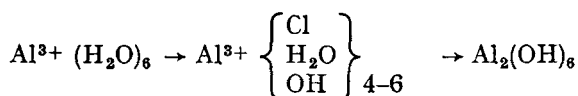
In an acid medium the problem we are faced with belongs to the well-studied class of substitution reactions of octahedral complexes, since the starting point consists in the hexahydrated form of Fe^{3+} or Al^{3+} and the final state in crystalline species in which the coordination number of the metal atom is unchanged.

According to Basolo and Pearson's treatment (1958), the intermediate stages between the precipitation mechanism and the deionization process may be considered as the intricate superposition of *nucleophilic substitutions* such as:

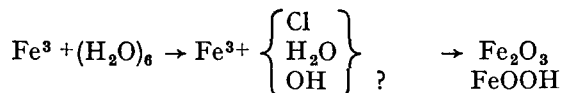


the metal atom being an *electrophilic* reagent which acquires electrons from the ligands acting as a *nucleophilic* reagent.

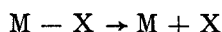
In most of the cases studied here, where the salts used were in the chloride form, the reactions leading to the crystalline species may be summarized as follows:



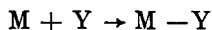
and



In the aluminic system, and probably also in the ferric one, the coordination number of the metal atom decreases in the intermediate step, which suggests that the reaction goes by a two-step mechanism in which the first step is a slow unimolecular heterolytic dissociation:



followed by a rapid coordination reaction of M with the substituting ligand Y



according to the nomenclature given by Hughes and Ingold this is a SN_1 mechanism. The polymerization reaction which leads to the solid crystalline species formation probably takes place when all the ligands but OH are expelled and accordingly when the octahedral coordination is restored. Edwards has proposed a two-parameter equation giving the rate constant k relative to that of water k_0 , E being a nucleophilic constant characteristic of the ligand and H the logarithm of the ordinary base constant relative to water as follows:

$$\ln k/k_0 = \alpha E + \beta H$$

For complex ion formation involving a small highly charged central atom, α is small and β is large. The values of E and H for some of the ligands employed in this work are given hereafter (Table 12).

TABLE 12.—DATA FOR E AND H ACCORDING TO BASOLO AND PEARSON

Donor	E	H
H ₂ O	0	0
SO ₄ ²⁻	0.59	3.74
Cl ⁻	1.24	-3.0
OH ⁻	1.65	17.48

For a given cation, substitution by OH⁻ is thus necessarily favored. According to the transition theory of reaction rates, a good estimate of the speed with which a chemical reaction occurs could theoretically be deduced from the energy required to form the activated complex. For the SN_1 type of substitution reaction, this could be done by estimating the energy difference between the six-fold and the lower intermediate coordination number.

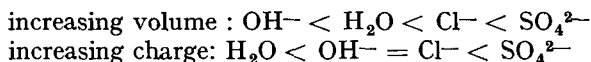
These calculations have been done in some limiting cases: results depend upon the number of electrons belonging to the metal atom. Fe³⁺ is characterized by five spin-uncoupled electrons, while Al³⁺ and Mg²⁺ do

TABLE 13.—EFFECT OF SIZES AND CHARGES OF LIGANDS ON THE RATE OF SN_1 REACTION

Increased negative charge of entering group	no effect
Increased size of entering group	no effect
Increased negative charge of leaving group	decrease
Increased size of leaving group	increase
Increased negative charge of other ligands	increase
Increased size of other ligands	increase
Increased size of the central atom	increase
Increased positive charge of central atom	increase

not contain such electrons. It follows that in any case and whatever the coordination change in the nature of the nucleophilic reaction, the activation is always higher for Fe^{3+} than for Mg^{2+} or Al^{3+} . All the predictions based on electrostatic considerations can be summarized as follows for the SN_1 reactions (see Table 13).

The ligands taken into consideration here may be classified as follows:



When chloride has to be expelled from the aluminum coordination sphere, a ligand of larger volume must be replaced by one of smaller volume without change in the electrical charge. The reaction rate decreases as compared with one of the reverse process, and for increased negative charge of the leaving group, such as the case of Cl^- and SO_4^{2-} , removal decreases the substitution rate.

These predictions are in good qualitative agreement with the observed facts. When the same process is compared for Fe^{3+} , which has an ionic radius larger than Al^{3+} , the reaction rate decreases. The opposite effect is observed when Mg^{2+} is compared to Al^{3+} . Brucite is obtained easily as compared with gibbsite and the ferric trihydrate is never obtained.

It may be concluded that the octahedral synthesis obeys quantitatively this oversimplified approach and, reciprocally, that the ligand exchange mechanism should be more deeply considered in the future for explaining this kind of mechanism.

REFERENCES

- Basolo, F., and Pearson, R. G. (1958) *Mechanism of Inorganic Reactions*: Wiley, New York.
- Brindley, G. W., and De Kimpe, C. (1961) Attempted low temperature synthesis of kaolin minerals: *Nature*, v.190, p.254.
- Calvet, E., Boivinnet, P., Noël, M., Thibon, H., Maillard, A., and Tertian, R. (1953) *Bull. Soc. Chim. France*, pp.99-108.
- De Flandre, A. (1963) Etude de l'évolution des gels de fer et d'aluminium et des gels mixtes en milieu dialysé: Mémoire, Université Catholique de Louvain.
- De Kimpe, C., Gastuche, M. C., and Brindley, G. W. (1961) Ionic coordination in aluminosilicic gels in relation to clay mineral formation: *Amer. Min.*, v.46, pp.1370-1381.
- De Kimpe, C., Gastuche, M. C., and Brindley, G. W. (1963) Low temperature synthesis of kaolin minerals: *Amer. Min.* (to be published).
- Delfosse, J. C. (1963) Réalisation d'un tonomètre et application des mesures tonométriques aux électrolytes mixtes et aux suspensions colloïdales: Mémoire, Université Catholique de Louvain.
- Feitchecht, W. (1942) Über die Bildung von Doppelhydroxyde Zwischen Zwei und dreiwertigen metallen: *Helvetica Chem. Acta*, v.25, pp.555-569.
- Feitchecht, W., and Gerber, M. (1942) Zur Kenntnis der Doppelhydroxyde und basischen Doppelsalze. III über magnesium-aluminum doppelhydroxyde: *Helvetica Chem. Acta*, v.25, pp.131-137.

- Frondel, C. (1941) Constitution and polymorphism of pyroaurite and sjögrenite groups: *Amer. Min.*, v.26, pp.295–315.
- Gastuche, M. C., and De Kimpe, C. (1959) Tentative de synthèse des argiles du groupe du kaolin dans les conditions normales de température et de pression: *Acad. Roy. Belg. Bull. Cl. Sci.*, v.45, pp.1087–1104.
- Gastuche, M. C., and Herbillon, A. (1962) Etude des gels d'alumine. Cristallisation en milieu désionisé: *Bull. Soc. Chim. France*, pp.1404–1412.
- Gastuche, M. C., and Fripiat, J. J. (1962) Acid dissolution techniques applied to determination of the structure of clays and controlled by physical methods: *Science of Ceramics*, ed. J. H. Stewart, Academic Press, London, pp.121–138.
- Gastuche, M. C., Fripiat, J. J., and De Kimpe, C. (1962) La genèse des minéraux argileux de la famille du kaolin. I. Aspect colloïdal. *Coll. Int. du C.N.R.S. Genèse et Synthèse des Argiles*, Paris, pp.57–65.
- Gastuche, M. C., and De Kimpe, C. (1962) La genèse des minéraux argileux de la famille du kaolin. II. Aspect cristallin: *Coll. Int. du C.N.R.S. Genèse et Synthèse des Argiles*, Paris, pp.67–81.
- Gastuche, M. C., Bruggenwert, T., and Mortland, M. M. (1964) Crystallization of mixed iron and aluminum gels: *Soil Sci.* (to be published).
- Gastuche, M. C., Fripiat, J. J., and Sokolsky, S. (1963) Fixation du phosphore par les hydroxides de fer et d'aluminium amorphes et cristallisés: *Pédologie* (to be published).
- Hénin, S., and Caillère S. (1961) Vue d'ensemble sur le problème de la synthèse des minéraux phylliteux à basse température: *Coll. Int. du C.N.R.S. Genèse et Synthèse des Argiles*, Paris, pp.31–43.
- Herbillon, A., and Gastuche, M. C. (1962) Synthèse et Genèse de l'Hydrargillite: *Compte-Rendus*, Paris., v.254, pp.1105–1107.
- Herbillon, A., and Gastuche, M. C. (1962) Etude des complexes kaolinite-hydroxide d'aluminium. Synthèse et Genèse des trihydrates cristallisés: *Bull. Group Fr. des Argiles*, v.14, pp.77–94.
- Longuet-Escard, J. (1951) Sur un aluminat de nickel hydraté: *Mem. Serv. Chim. de l'Etat*, v.2, pp.187–193.
- Richards, L. A., and Ogata, G. (1958) Thermocouple for vapour pressure measurements in soil systems at high humidity: *Science.*, v.128, No. 3331, pp.1089–1090.
- Tilley, L. A., Megaw, H. D., and Hey, M. H. (1934) Hydrocalumnite ($4 \text{ CaO}, \text{Al}_2\text{O}_3, 12\text{H}_2\text{O}$), a new mineral from Scawt Hill Co., Antrim: *Min. Mag. and Jour. of the Min. Soc.*, v. XXIII, No. 147.