

KAOLINITE SYNTHESIS. II. A REVIEW AND DISCUSSION OF THE FACTORS INFLUENCING THE RATE PROCESS

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Abstract—Kaolinite is synthesized in approximately the same time in three temperature ranges: (1) from 200–250° to 350–400° (hydrothermal processes); (2) from 120 to 175° (semihydrothermal ones); (3) at ordinary temperature. It is thus evident that the rate process cannot be explained by the Arrhenius equation only, but is explained well by considering that kaolinite formation obeys the laws of crystal growth. It occurs only in slightly supersaturated solutions in which the nucleation process is possible and in which a slow and regular rate of growth has been insured. Concentrations calculated from the thermodynamical equilibria correspond to those of the experimental conditions for the low temperature processes. For the higher temperature ones, a similar relationship is delineated, at least as far as the thermodynamical treatment can be carried out.

Key Words—Hydrothermal, Kaolinite, Synthesis, Thermodynamic.

INTRODUCTION

Clay minerals and related oxides are found in all geographic locations where the average temperature exceeds 5°C. According to general field observations, they form at low temperature (<30°C) from aqueous solutions which contain essentially the major constituents and are the result of weathering processes. The nature of the clay mineral is related to the physicochemical conditions of weathering (see, for example, Keller, 1970). From studies of artificial rock weathering, Pedro (1964) also considers that the nature of the clays depends essentially on physicochemical factors and is mainly independent of petrographical factors.

The large amount of clay minerals present in nature and their widespread distribution indicates that their formation must proceed easily, but many experiments to reproduce these processes artificially have given deceptive results. Amorphous to very poorly crystallized phases are obtained which do not evolve towards any crystalline phase, even after long aging. Only recently have experiments given positive results.

This paper discusses the conditions for the synthesis of kaolinite and is limited to the system Al_2O_3 - SiO_2 - H_2O . However, some reactions in 'acid' and 'alkaline' media also will be mentioned.

THE TIME FACTOR VERSUS THE TEMPERATURE FACTOR

Clay minerals are easily and rapidly obtained from hydrothermal experiments that elucidate the occurrence of deposits from hydrothermal origin but, contrary to what has been stated in most geological treatises,

these experiments do not readily explain the very large amount formed at low temperatures. The most common explanation has been to consider that the processes involved obey the Arrhenius equation:

$$k_1 = A \exp(-E/RT) \quad (1)$$

in which A is the frequency factor, R the gas constant, E the activation energy for the reaction, and k_1 its rate at the absolute temperature T. The general failure to obtain crystallization at low temperature is then attributed to the processes occurring at an immeasurably slow rate requiring geological periods of time.

That such an argument is not relevant is unambiguously proved by the recent successful low temperature synthesis of kaolinite (La Iglesia and Van Oosterwyck-Gastuche, 1978, and references in Table 4).

Hydrothermal systems

Evidence that the process is far more complex is obtained from the very first hydrothermal experiments (Noll, 1935, 1936, 1944) which show that not only the rate but also the type of the crystallization changes with increasing the temperature, the 1:1 layer structures forming at lower temperatures than the 2:1 ones. Although this result was obtained by all the investigators, the interpretation of their experiments nevertheless is not easy, the data being "numerous and conflicting" (Roy and Osborn, 1954). Furthermore, the conditions existing at high temperature are different in many aspects from those at low temperature: in those solutions (often under vapor phase), the pH does not have the same meaning, the density of the water, its dielectric constant, and the hydration of the ions have changed;

Table 1. Procedures utilized for the hydrothermal synthesis starting from gels.

Author	Starting material	Technique	Time (days)	Crystallizations obtained
Ewell and Insley (1935)	a) Al-Si gels coprecipitated from Al sulfate and Na silicate, neutralized, dried washed, and ground. Still contain small amounts of Na b) ground mixtures of dried silica gel with dried γ -Al ₂ O ₃ or boehmite	bomb capable of withstanding 200 bars pressure and 400°	7-10	boehmite kaolinite dickite
Noll (1935-36, 1944)	a) Al-Si gels coprecipitated from Al chloride and Na silicate neutralized, dried washed, and ground, (method of Schwarz and Brenner) b) also ground mixtures of oxides	stirring autoclave t° 200-500° p 8-40 bars	from 1 to 150 hr	boehmite kaolinite pyrophyllite
Roy and Osborn (1954)	a) Al-Si gels prepared after the method of Ewell and Insley	bomb capable of withstanding 3.500 bars and 600°	from 40 s to 6 months	kaolinite hydralsite Al-montmorillonite pyrophyllite
also Roy (1952)	b) some purified by electrodiálises c) mixture of ground oxides, considered "very unsatisfactory and dangerous"	material in golden tubes		
De Kimpe (1967)	Al-Si gels prepared by slow co-hydrolysis of ethyl silicate and Al-isopropoxide dried at 70° (method of Leonard et al., 1964)	Pyrex tubes t° 175° HCl 0.1 N, H ₂ O, NaOH 0.1 N	10	pseudoboehmite in HCl phillipsite or chabazite in NaOH
De Kimpe (1969)	same procedure Al ₂ O ₃ /Al ₂ O ₃ + SiO ₂ = 0.4	Pyrex tubes t° 175° NaOH 0.1 N, continuous agitation pH 6-6.5	8-16	kaolinite
Rodrique, Poncelet and Herbillon (1972)	Al-Si gels prepared after the method of Leonard et al. (1964)	stainless steel autoclave material in golden tubes t° 175-250° p 8.8-39.2 bars	7	boehmite pseudoboehmite kaolinite
De Vijnck (1973, 1976)	Al-Si gels prepared after the method of Leonard et al. (1964)	Autoclave Andreas Hoffer, standing 500 bars and 400° C material in golden crucibles	1-9 generally 7	boehmite pseudoboehmite kaolinite pyrophyllite cristobalite
Eberl and Hower (1975)	Al-Si gels prepared from Al nitrate or Al metal and mixed with "ludox" sols, after the method of Luth and Ingamels (1965)	1) small wedged golden tubes at 2000 bars and 250-343° 2) larger teflon containers 1-5 bars, 100-152° C	from 20 to 101	1) kaolinite (ordered) kaolinite (dis-ordered) pyrophyllite hydralsite 2) disordered kaolinite

N.B. All the pressure units have been expressed in bars, making the approximation 1 bar = 1 atm.

also silica, very poorly soluble at low temperature, becomes very soluble.

Another important statement is that the rate of the reaction still depends on the nature of the starting materials, either crystals, ground oxides, gels, or even different kinds of gels (Roy, 1962; Roy in Rayner, 1962). For instance, muscovite is generated from anhydrous corundum and sanidine in a few minutes, while a gel takes hours to react (Roy, 1962). In a general way, gels (in which the mixture of the reacting species occurs at

the atomic scale) are preferred to crystals or to mixtures of ground oxides (Roy, 1962).

Table 1 reports the different procedures from gels and Table 2 the main results obtained. Both illustrate a general lack in the standardization of the procedures inducing discrepant results. It is of interest to notice that, even when starting from the same kind of gel, results are different according to the device utilized (compare the results from De Kimpe, 1967, 1969 with those of Rodrique et al., 1972 and of de Vijnck, 1973, 1975).

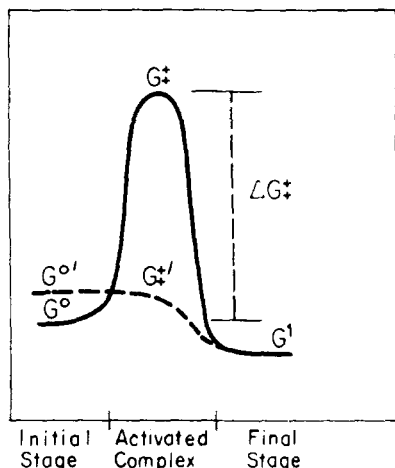


Fig. 1. Example illustrating changes in reaction rates explained by the theory of absolute rate processes. In the first case, the reaction although theoretically possible ($G^1 - G^0 < 0$) does not occur at ordinary temperature on account of the large energy barrier ΔG^{\ddagger} . In the second case, the starting material has a free energy $G^{0'}$. The reaction is thus theoretically possible too, but will occur in this case at ordinary temperature because the energy barrier ΔG^{\ddagger} has disappeared.

In a general way, the temperature of the synthesis of kaolinite from gels ranges from about 250° to 400°C, and its rate increases with increasing temperature, at least within a certain range (Rayner, 1962), but lower rates have been obtained without any satisfactory explanation (200°, Rodrique et al., 1972; 180°, Rayner, 1962; 175°, De Kimpe, 1969; even 150°, Roy and Osborn,

1954; Eberl and Hower, 1975). We shall not consider here the important (and also discrepant) changes induced by the introduction of cations (see for instance Noll, 1935, 1936, 1944; De Vijnck, 1975, 1976; Eberl and Hower, 1975) nor of CO₂, of great importance in the natural hydrothermal media (see Tugarinov and Naumov, 1973, and experiments of Lagache, 1966; Tchoubar and Oberlin, 1966, etc.).

Evidently the parameters involved in such reactions are far too complex to be explained by the Arrhenius equation alone.

Semihydrothermal systems

The general utilization of gels in synthesis studies excluded any investigation of the influence of the starting materials. A preliminary attempt, although mainly qualitative, was made first by De Kimpe et al. (1964). It was based on the theory of absolute rate processes (Glasstone et al., 1941; Laidler, 1950) which considers that at least one intermediate stage exists between the initial and the final phase, the so-called "activated complex" in which the structural reorganization necessary to create the final state occurs. Even if the free energy change between the initial and final states is negative and the reaction, therefore, is theoretically possible, it may be prevented by the positive energy required to attain this activated state and will occur only when it is overcome (see Figure 1).

The rate process for this reaction is given by the expression:

Table 2. Results of the hydrothermal synthesis starting from gels for varying Al₂O₃/SiO₂ ratios.

Author	t°C	P (bars)	Molar ratio Al ₂ O ₃ /SiO ₂ (H ₂ O constant)					
			1:0	>1:2	1:2	1:4	<1:4	0:1
Noll (1935-36, 1944)	250	41	Bh	K + Bh	K	K	K + SiO ₂ (am)	SiO ₂ (am)
	300	87	Bh	K + Bh	K	K	K + SiO ₂ (am)	SiO ₂ (am)
	350	168	Bh	K + Bh	K	K	K + SiO ₂ (am)	SiO ₂ (am)
	400	300	Bh	K + Bh	P + Bh + K	P	P + SiO ₂ (am)	SiO ₂ (am)
	500	530-540	C	K + Bh	P + ?	P	P + SiO ₂ (am)	SiO ₂ (am)
			Approximate molar ratio			Al ₂ O ₃ /SiO ₂ (H ₂ O constant)		
			1:0	1:1	1:2	1:3	—	—
Rodrique, Poncelet and Herbillon (1972)	175	8.8	Bh	poor Ps Bh	Am	Am	—	—
	200	15.3	Bh	poor Ps Bh	well cryst. K	well cryst. K	—	—
	220	22.9	Bh	poor K	well cryst. K	poor K	—	—
	250	39.2	Bh	well cryst. K	well cryst. K	poor K	—	—
			Molar ratio			Al ₂ O ₃ /SiO ₂ (H ₂ O constant)		
			—	1:1	1:2	1:4	—	—
De Vijnck (1973, 1976) (7 days, results from 1976)	256	45	—	Ps Bh	K	K	—	—
	346	160	—	Bh	K	P	—	—
	420	450	—	H	H	P	—	—
	500	450	—	H	H	P + H	—	—
	600	450	—	M	M + C	C + M	—	—
650	450	—	M + C	M + C	M + C	—	—	

Symbols utilised: K: kaolinite; Bh: boehmite; Ps Bh: pseudoboehmite; Am: amorphous; P: pyrophyllite; C: cristobalite; M: mullite; H: hydralsite.

Molar ratios from Rodrique et al. have been transformed in order to standardize the results.

Table 3. Results from semihydrothermal synthesis—influence of the structure of the starting materials.

Authors	Starting materials		t°C	Reaction medium	Time days	Crystallizations obtained
	Al source	Si source				
Brindley and De Kimpe	large gibbsite crystals (Alcoa)	hydrolyzed ethyl silicate	175°	HCl, pH 1,5 Pyrex containers	10	lathlike kaolinite
Gastuche and De Kimpe (1962)	large gibbsite crystals (Alcoa)	hydrolyzed ethyl silicate	(1) 150° (2) 175°	HCl, pH 1,5 Pyrex containers	10	(1) hydrated kaolinite with traces of chlorite (2) lathlike kaolinite
De Kimpe, Gastuche and Brindley	(1) Alcoa gibbsite (2) small-sized gibbsite (3) bayerite (4) "pregibbsite" (5) AlCl ₃ ·6H ₂ O (6) fresh Al-gel precipitated on muscovite (7) boehmite	hydrolyzed ethyl silicate or Ludox (no difference)	170–175°	HCl, pH 1,5 (1, 2, 3, 4, 5) pH 6 to 3 (6) Pyrex containers constant vol of liquid (16 ml)	10	(1) hydrated kaolinite, lathlike kaolinite (2) { (3) } hexagonal kaolinite (4) { (5) } amorphous, traces of hex. kaol. (M.E.) (6) small amounts of hydrated kaolinite (7) no reaction
De Kimpe and Fripiat (1968)	H-exchanged zeolites of different pore sizes		175°	HCl N/10 Pyrex containers HCl N/10 gold capsules	10	zeolites only react into kaolinite when Al-H-treated in order to give Si-O-Al ^{VI} units great difference between the reaction temperatures with the different containers
Poncelet and Brindley (1967)	(1) Na and Al montmorillonites (2) montm. interlayered with Al (OH) (3) vermiculite treated with Al(OH) layers (4) hectorite treated with Al(OH) layers (5) fluohectorite treated with Al(OH) layers		175–240°	(a) HCl N (b) HCl N + AlCl ₃ (c) HCl pH 4,8 (d) H ₂ O (e) 0.1 N NaOH sealed gold capsules	7–28	Large amounts of well crystallized hydrated kaolinite is obtained only from (2) in the different media at 220–240°, in various prop. No 7 Å phase with (3) (4) (5) traces with (1) at 220–230°; no reaction at 175°
Dennfeld, Siffert and Wey (1970)	gibbsite of different sizes gibbsite ground down to different degrees of amorphization reactions with complexing organic acids (1) salicylic (2) tartaric (3) citric (4) oxalic	amorphous SiO ₂	135–200°	1 ml org. acid 12 ml H ₂ O in a 17 mol vol container	7–21	200°, 7d. no 7 Å phase with (1) 7 Å phase increasing from (2) (3) (4) 135°, 14 d. 7 Å phase from small sized gibbsite only in (4) 175°, 14 d. 7 Å phase from ground gibbsite also in aqueous medium

$$k_1 = \alpha \frac{kT}{h} e^{(-\Delta G_{\ddagger}^{\ddagger}/RT)} \quad (2)$$

and, therefore, is related to $\Delta G_{\ddagger}^{\ddagger}$ (the free energy of formation for this complex) and to T (the absolute temperature); the other parameters are the classical constants (k , h , R) and α , a coefficient of transmission approximating 1.

The rate process, depending finally only on $\Delta G_{\ddagger}^{\ddagger}$ and T, can be increased in two ways: either by increasing the absolute temperature T or by decreasing the free energy of formation of the "activated complex," $\Delta G_{\ddagger}^{\ddagger}$. The classical procedure has been to increase the temperature, but it could be achieved as well by decreasing

the barrier $\Delta G_{\ddagger}^{\ddagger}$ by a convenient choice of starting materials.* These may be chosen so that the variation of free energy of the reaction itself becomes more negative, thus rendering easier the formation of the final state.

In fact, syntheses in a temperature range from 120 to

* Glasstone et al., 1941, observed: "When a reaction occurs between complex molecules and there is a considerable re-arrangement of energy among the degrees of freedom, there is a decrease of entropy in the formation of the activated complex." The enthalpy of the reaction will probably also be reduced by a proper choice of the starting materials. This "preorganization" can also be related to apitaxial heteronucleation.

Table 4. Low temperature synthesis.

Authors	Starting materials	pH	t°	Time	Crystallizations obtained (X-rays)
Harder (1970)	coprecipitated Al-Si gels from very dilute Al and Si solutions	4.5-5	20	1-3 months	kaolinite
Kittrick (1970)	0.2-5 μm fractions of montmorillonite slightly supersaturated towards kaolinite	2.60-3.47	20	3-4 years	kaolinite (well crystallized)
Linares and Huertas (1971)	slow destruction of an Al-fulvic complex in dilute Si-rich solutions. $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratio varies	2-9	20	1 month	kaolinite (poor) gibbsite bayerite pseudoboehmite
La Iglesia and Martin Vivaldi (1972)	slow destruction of an Al-fulvic complex in dilute Si-rich solutions	4-8	20	2 months	kaolinite (poor)
La Iglesia, Martin Caballero and Martin Vivaldi (1974) La Iglesia et al. (1976)	homogeneous precipitation through hydrolysis of feldspars in dilute Si and Al-rich solutions	4	20	2 months	mica kaolinite smectite
La Iglesia and Martin Vivaldi (1975)	homogeneous precipitation through reaction of dilute Si and Al solutions with two anionic resins in OH^- forms	5.7-6.6	20	2 months	halloysite kaolinite bayerite crystallization varies with Al-source (Al acetate or chlorite) and the resin
La Iglesia and Serna (1974)	homogeneous precipitation through reaction of dilute Si and Al solution with several cationic resins in H_3O^+ form	8.2	20	2 months	positive results with the carboxylic resin alone: kaolinite and bayerite
Hem and Lind (1974) Lind and Hem (1975)	very dilute solutions of Al and Si in solutions containing quercetin	6.5	20	6-16 months	X-ray amorphous. Kaolinite at E.M. and E.D.
La Iglesia and Van Oosterwyck-Gastuche (1978)	slow migration of dilute Na_2SiO_3 solutions	4.5-5	60	2 months	halloysite kaolinite

N.B. The range of dilution is approximately from 1-100 ppm in SiO_2 and Al_2O_3 .

175° have been performed from structurally favorable materials such as: gibbsite, bayerite, "pregibbsite," Al gel on muscovite (De Kimpe et al., 1964), gibbsite ground down to different stages of amorphization (Denfeld et al., 1970), pretreated zeolites with Si-O-Al^{IV} chains (De Kimpe and Fripiat, 1968), Al-OH interlayered montmorillonite (Poncelet and Brindley, 1967).

Results from Table 3 show that all the starting materials are characterized by the presence of Al in sixfold coordination, while those containing Al^{IV}, such as the untreated zeolites (De Kimpe and Fripiat, 1968) or most of the gels (De Kimpe, 1968; Rodrique et al., 1972; De Vijnck, 1975, 1976; see Tables 1 and 2), reacted at higher temperatures.

The lack of data on the thermodynamic constants prevents any quantitative treatment but it is evident that the "preorganization" of the starting materials can influence favorably the rate of the crystallization process at temperatures above 100°.

Low temperature processes

The influence of "preorganization" in low temperature processes was shown first in experiments using "preorganized" materials in very definite conditions and even then the yields were often poor (Caillère and Hémin, 1962; Fripiat and Gastuche, 1963; Gastuche, 1964). An important advance in their quantitative treatment was obtained from the calculations of Garrels and Christ (1965) that deduced the concentrations at equilibria from the standard free energy values for the gibbsite-water, kaolinite-water, and kaolinite-gibbsite systems. An attempt to complete those diagrams by considering the free energy values of the corresponding gel phases has been performed recently by La Iglesia and Van Oosterwyck-Gastuche (1978, see Part I).

The concentrations in Al³⁺ and H_4SiO_4 able to crystallize to kaolinite are *extremely low*, much lower than believed by former experimenters, so that both the

Table 5. Dependence of the temperature on the water volume (Experiments from Eberl and Hower, 1975).

t°	Approximate Al ₂ O ₃ /SiO ₂ molar ratio (H ₂ O constant)*			
	1.5:2	1:2 (XVI)	1:2 bis (XV)†	1:4
(1) Experiments in small wedged tubes. Time 18–169 days (within brackets: time in days) 2000 bars—30 mg of powdered material in gold tubes (3.05 mm o.d., 2.54 mm i.d.) cont. 35 μl water				
250–253	—	K (ord) (18)	K (ord) (167)	K (dis) (99)
2 85	K (ord) + Bh (28)	—	K (ord) (74)	—
310	—	—	—	—
330	—	—	K (ord) (74)	K (dis) (12)
337	—	—	—	P (74)
347	—	—	—	—
358	—	—	K (ord) (28)	—
360	—	K (ord) (28)	—	—
363	—	K (ord) (16) (175 bars)	—	—
379	—	—	—	P + Q
(2) Experiments in large teflon vessels, time 20 to 101 days, 100° 1 bar, 126° 2 bars, 152° 5 bars 100 mg of powdered material in 25 ml water				
100	—	—	—	no reaction (101)
126	—	—	—	tr K ? (85)
152	—	K (78)	no reaction (82)	K (dis) (101)
155	—	—	K (poor) (20)	K (poor) (20)
158	K (sl. ord) (60)	—	—	—

* The Al₂O₃/SiO₂ ratios have been transformed and approximated to standardize the data under discussion.

† XV and XVI are two gels with the same Al₂O₃/SiO₂ ratio but XV contains mullite and XVI, corundum.

Only the results of the Al₂O₃·SiO₂·H₂O systems have been considered here.

Symbols: K (ord): kaolinite, ordered; K (sl. ord): kaolinite slightly ordered; K (dis): disordered kaolinite; K (poor): poor kaolinite; Q: quartz; P: pyrophyllite.

failures and the successful attempts find a logical explanation, related to the concentration of the working solutions. It thus appears clearly that the formation of kaolinite obeys the general laws of crystal growth; it forms only from solutions slightly supersaturated towards the crystal. The concentrations can be calculated easily from the thermodynamical equilibria and experiments set up under these conditions give positive results (Table 4).

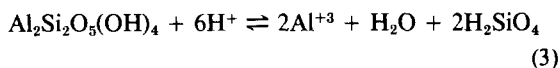
DISCUSSION

For the same conditions of time of reaction, concentration, and temperature, these low temperature reactions do not proceed at the same rate. Other parameters discussed by La Iglesia and Van Oosterwyck-Gastuche (1978, see Part I) enter into the process.

As far as higher temperature processes are concerned, the analysis of the results shows that the temperature of the synthesis decreases not only when starting from "preorganized" materials, but also for the same materials when the volume of the solution increases. This has been best evidenced in recent experiments from Eberl and Hower (1975) as illustrated in Table 5.

Coming back to other experiments previously performed on gels of the same composition, Figure 2 shows that a rough linear relationship exists between the log

of the concentration in kaolinite (expressed in H₄SiO₄) and the temperature. These data have been related to the solubility values at high temperatures calculated by Helgeson (1969). The results show that the crystallization of kaolinite occurs in approximately the same conditions of supersaturation at higher and at lower temperatures and that the only difference is its increased solubility at high temperatures. The solubility lines in the lower part of the diagram have been calculated from log K values from Helgeson (1969) for the equation:



The calculation goes up to 300°C; reactions below these temperatures, according to Helgeson, are independent of the water pressure. The homogeneity of the data obtained here, although performed by different experimenters working in different conditions, seems to confirm it. However, this is certainly not the case at higher temperatures, as evidenced by Ostapenko et al. (1975) from experiments on kaolinite decomposition, that depended to a large extent on the water vapor pressure. The comparison between the theoretical calculations and the experimental data cannot be carried very far, because those experiments have not been carried out in order to control the true thermodynamical constants involved in the reactions on the one hand

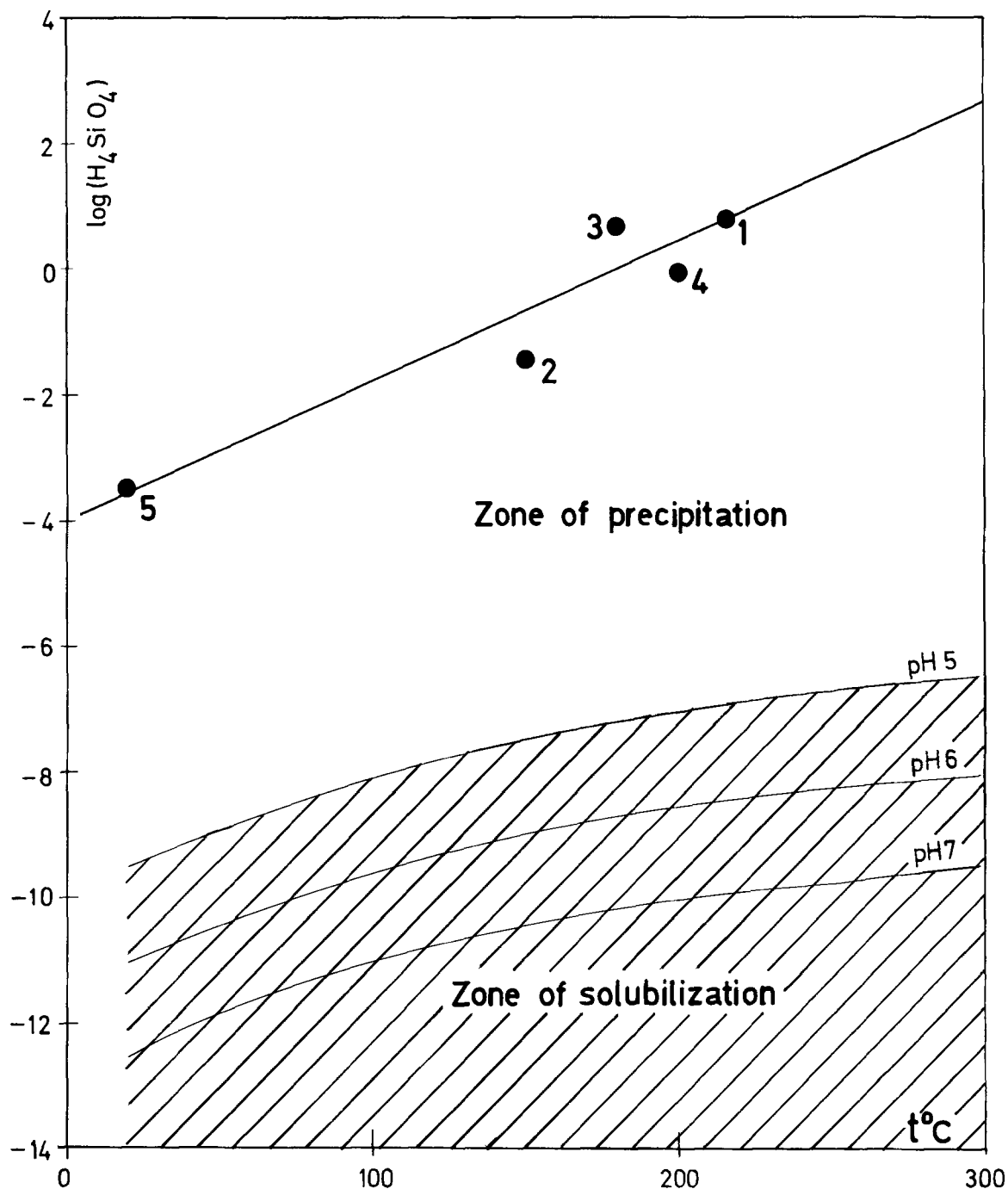


Fig. 2. Variation in the log in kaolinite concentration expressed in (H_4SiO_4) related to the temperature: (1) and (2) are respectively data from Eberl and Hower (1975) from experiments in small welded tubes (1) and in large teflon vessels (2); (3) are data from Rodrique et al. (1972); (4) those from Rayner (1962); (5) those from Harder (1970). The temperature considered here is the lower one in which kaolinite appears in the semihydrothermal runs, and the one at which the low-temperature runs have been carried out. Lower lines are calculated values for the solubility of kaolinite taken from Helgeson (1969).

and, on the other hand, because many still uncontrolled assumptions are made in the theoretical calculations. New sets of experiments should be performed systematically in order to make further progress.

CONCLUSION

As far as a comparison can be made between high- and the low-temperature syntheses, it is considered

that below 300° the main factor governing the synthesis is the concentration required to induce the nucleation process which must be slightly supersaturated towards the crystal. The only difference, when increasing the temperature, appears to be the solubility of the kaolinite that increases and may thus crystallize from more concentrated solutions.

Factors of "preorganization" also influence favorably the rate process, as outlined; these are mainly epitaxial heteronucleation processes.

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Резюме- Каолинит был синтезирован примерно за одинаковое время при трех диапазонах температур: 1) от 200-250° до 350-400° (гидротермальные процессы); 2) от 120 до 175° (полу-гидротермальные процессы); 3) при обычной температуре. Это свидетельствует, что скорость процесса не может быть объяснена только уравнением Аррхениуса, но хорошо объясняется, если полагать, что формирование каолинита подчиняется законам роста кристаллов. Это наблюдается только в слегка пересыщенных растворах, в которых возможен процесс образования центров кристаллизации и в которых обеспечивается низкая и нормальная скорость роста кристаллов. Концентрации, вычисленные из термодинамических уравнений равновесия, соответствуют уравнениям, полученным из экспериментальных условий для низкотемпературных процессов. Для высокотемпературных процессов установлены аналогичные взаимоотношения, по крайней мере до тех пор, пока может проводиться термодинамическая обработка.

Kurzreferat- Kaolinit wird innerhalb derselben Zeit in drei Temperaturbereichen synthetisiert: (1) von 200-250° bis 350-400° (hydrothermisches Verfahren); (2) von 120° bis 175° (semihydrothermisches); (3) bei gewöhnlicher Temperatur. Es ist daher klar, daß das Geschwindigkeitsverfahren nicht alleine mit der Arrheniusgleichung erklärt werden kann, aber es kann gut erläutert werden indem man in Betracht zieht, daß die Kaolinitbildung die Gesetze des Kristallwachstums einhält. Es kommt nur in leicht übersättigten Lösungen vor, in welchen Nukleation stattfinden kann und in welchen langsames, regelmäßiges Wachsen gesichert ist. Konzentrationen, welche von den thermodynamischen Gleichgewichten errechnet werden, stimmen mit den experimentalen Bedingungen für das Verfahren bei niedriger Temperatur überein. Für die Verfahren bei höherer Temperatur kann eine ähnliche Verwandtschaft abgeleitet werden, zumindest solange wie die thermodynamische Behandlung ausgeführt werden kann.

Résumé-La kaolinite est synthétisée à peu près en même temps dans trois étendues de température: (1) de 200°-250° à 350-400° (procédés hydrothermiques); (2) de 120 à 175° (procédés semi-hydrothermiques); (3) à température normale. Il est donc évident que le procédé de vitesse ne peut pas être expliqué par l'équation d'Arrhénius uniquement, mais est bien expliqué en considérant que la formation de kaolinite suit les lois de croissance de cristaux. Cette formation ne survient que dans des solutions à peine super-saturées dans lesquelles le procédé de nucléation est possible et dans lesquelles une vitesse de croissance lente et régulière est assurée. Les concentrations calculées d'après les équilibres thermiques correspondent à celles des conditions expérimentales pour les procédés à basse température. Pour ceux à haute température, une parentée similaire est esquisée, du moins jusqu'au point où le traitement thermodynamique peut être exécuté.