

KINETIC STUDIES ON MONTMORILLONITES AND NONTRONITE BY THE ACID-DISSOLUTION TECHNIQUE¹

By

BERNARD OSTHAUS

Gulf Research & Development Company, Pittsburgh, Pennsylvania

ABSTRACT

Several montmorillonites and a nontronite were digested in hydrochloric acid at constant temperature for various periods of time. Soluble iron, aluminum, magnesium, and in two samples titanium, were determined for each digestion period. Rate of solution curves were obtained by plotting the logarithm of the percent of the residual ions against time. In general, the solution curves were straight lines or curves that could be resolved into two straight lines. From the interpretation of the dissolution curves, it was possible to determine the amount of the ions in octahedral and tetrahedral coordination. For some of the samples, the rate curves also gave the amount of iron and/or aluminum extraneous to the clay lattice. The amount of silicon in the clay lattice was calculated using the experimentally determined octahedral cations, substituted tetrahedral cations if any, and the exchangeable cations assuming 44 charges per unit cell. The distribution of cations in lattice layers indicates that the eight montmorillonites are substantially dioctahedral. Two of the samples showed the presence of iron in tetrahedral coordination while all the samples showed extraneous silicon. The presence of extraneous silicon, iron, and aluminum in purified samples indicates that formulas derived from bulk chemical analyses can be inaccurate.

The dissolution of the ions from the clay lattice determined at several different temperatures in one sample and at two acid concentrations in another sample is in agreement with chemical kinetic principles and is a first-order reaction. The rate constant for the acid dissolution reaction increased proportionately with the acid concentration.

The activation energies were determined for the solution of iron and aluminum in montmorillonite from Polkville, Mississippi, and nontronite from Garfield, Washington, using Arrhenius' Law. In both samples the activation energies (17 to 18 kilocalories per mole) were the same. In the nontronite sample the activation energies were identical for what have been interpreted as octahedral and tetrahedral ions.

INTRODUCTION

For many years the structural formulas of montmorillonites have been calculated from the chemical analyses of samples that have often included extraneous material. As pointed out by Kelley (1945) the presence of impurities influences the calculated distribution of cations in lattice layers. Ross and Hendricks (1945) realized the difficulties in obtaining pure samples or correcting the analytical data of impure samples. Kerr and others (1951) derived chemical formulas for several montmorillonite-type specimens, but the mineral impurities present were only estimated.

The presence of impurities seriously affects the calculated composition of the clay lattice and particularly the tetrahedral layer since any substitution for silicon is derived from theoretical calculations. For many years aluminum was

¹ Publication authorized by Executive Vice-President, Gulf Research & Development Company.

considered as the only element substituting for silicon in montmorillonite. Thus, the composition of the tetrahedral layer is subject to the cumulative errors of the chemical analysis of impure minerals.

Brindley and Youell (1951) were the first to attempt the direct chemical determination of octahedral and of tetrahedral aluminum in layer silicates by an acid-dissolution technique. Karsulin and Stubican (1954) also applied the same method to several synthetic montmorillonites and experimentally determined the amounts of aluminum in octahedral and in tetrahedral coordination.

The author (Osthaus, 1954) also applied the acid-dissolution technique for the direct determination of tetrahedral and octahedral ions in a nontronite and a montmorillonite. Although the aim of the acid-dissolution method was similar to that of Brindley and Youell and of Karsulin and Stubican, the method of interpreting the results was significantly different. It was observed that the logarithms of the percents of residual iron, aluminum, and magnesium when plotted against time gave either straight lines or curves. The straight lines obtained in the Polkville sample were interpreted as representing the dissolution of iron and aluminum in only octahedral coordination. The curves of iron and aluminum obtained with the Garfield, Washington, nontronite were interpreted as representing the simultaneous solution of octahedral and tetrahedral ions but at different rates, that of the octahedral ion being considerably more rapid. When the digestion was continued for a sufficient time, practically all the octahedral ions passed into solution; further acid digestion then represented the solution of tetrahedral ions. Resolution of the acid-dissolution curve gave the amount of the ion in tetrahedral coordination and in octahedral coordination. Thus, the acid-dissolution curves (Osthaus, 1954) of the nontronite sample suggested that this mineral contained considerable iron in addition to aluminum in tetrahedral coordination, in spite of the fact that enough aluminum was present to fulfill the silicon deficiency.

In view of the uncertainties and difficulties experienced in the study of impure clay materials and in acid-dissolution of layer silicates, the author continued the investigation of these problems using chemical kinetic principles. The effect of impurities on the distribution of cations in lattice layers has been studied and the amount of silica or silicon-bearing impurity calculated. In addition, the apparent activation energies have been determined for the solution of iron and aluminum in nontronite from Garfield, Washington, and montmorillonite from Polkville, Mississippi.

MATERIALS STUDIED

All but two of the montmorillonite specimens used in this investigation were from the series of bentonites collected by Kerr and others (1951). The other two specimens from Plymouth, Utah, and Merritt, British Columbia, have been previously described by Earley, Osthaus, and Milne (1953). The clay minerals were sodium saturated as completely as possible with 1 *N* neutral sodium acetate in a conventional base-exchange procedure and separated by a Sharples supercentrifuge into several particle-size fractions. The particle size of the clay minerals used in the acid-dissolution studies was thought to be of the order of 0.2 to 0.05 microns.

EXPERIMENTAL PROCEDURES

Chemical analyses were made on the eight montmorillonite specimens and the nontronite sample by accepted procedures. Exchangeable cations also were determined on the eight montmorillonite specimens.

Acid-dissolution studies were made on approximately ten half-gram samples of clay which were equilibrated with laboratory air, weighed, and transferred to platinum-foil strips until needed for the digestion in acid. It was necessary to weigh all the samples of each specimen at one time to avoid the effects of changing humidity. The samples were transferred from the platinum strips to 200-ml flat-bottomed Vycor flasks as required. The Vycor flasks were connected to

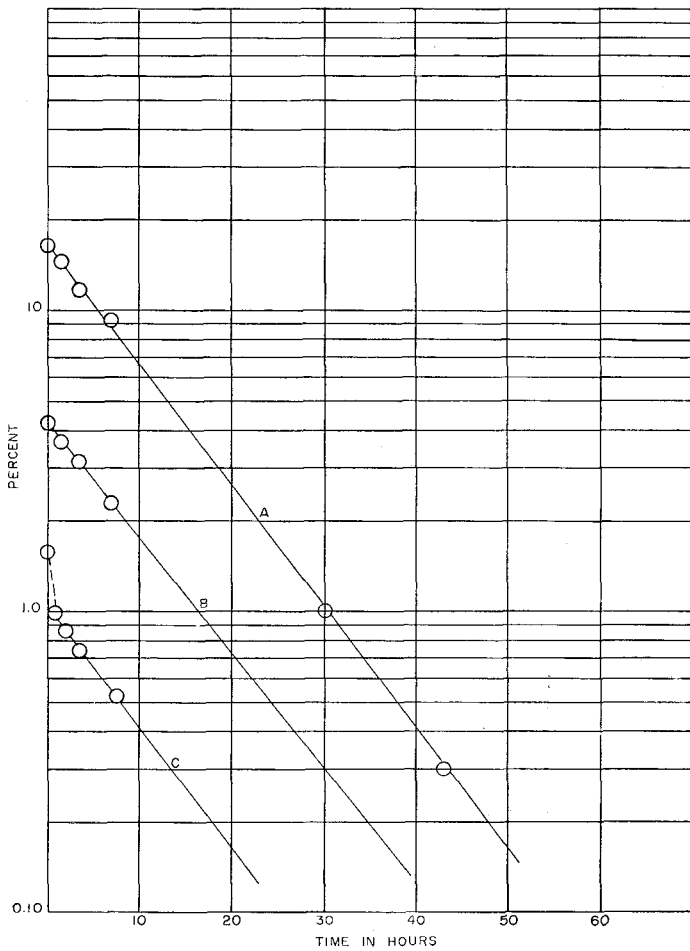


FIGURE 1.—Dissolution curves of montmorillonite, Polkville, Miss. *A*, Octahedral aluminum. *B*, Octahedral magnesium. *C*, Octahedral iron.

water-cooled reflux condensers by ball and socket ground glass joints. Just before clamping the flasks to the condensers, 100 ml of either 10 or 30 percent by volume hydrochloric acid was introduced into the flasks.

The strength of acid and digestion temperature will be discussed later under factors affecting dissolution. The bulb sections of the flasks were submerged in a constant-temperature oil bath for various periods of time and the temperature of the clay-acid mixture was measured by inserting a mercury thermometer into the mixture. At the end of each digestion period, the flasks were removed from the oil bath and quickly cooled. The clay-acid suspensions were filtered, and filtrates were retained for chemical analyses. For the short digestion periods, the filtrates were analyzed for soluble iron, aluminum, and magnesium. The amount of each ion remaining undissolved was calculated by subtracting the percent soluble from the total percent in the sample. If the samples were digested for long periods of time, it was advantageous to determine the small amounts of undissolved iron, magnesium, and aluminum directly from the insoluble residues.

The acid-dissolution curves were obtained by plotting the logarithm of the percent of the undissolved ion, expressed as the oxide, against time.

RESULTS AND DISCUSSION

Chemical Analyses

The bulk chemical analyses of the eight montmorillonite samples and a nontronite are given in Table I.

TABLE I—CHEMICAL ANALYSES¹ AND EXCHANGEABLE CATIONS¹ OF MONTMORILLONITES AND NONTRONITE

	Polkville, Miss.	Santa Rita N. Mex.	Otay, Calif.	Merritt, B. C.	Belle Fourche, S. Dak.	Plymouth, Utah	Clay Spur Wyo.	Amory, Miss.	Garfield, Wash. ²
SiO ₂	53.42	58.10	57.80	60.00	56.80	54.25	54.90	55.39	44.00
Al ₂ O ₃	16.40	17.15	16.25	14.73	21.32	17.60	20.30	19.20	6.41
Fe ₂ O ₃	1.58	1.02	1.10	3.60	4.07	4.31	3.70	6.77	31.90
TiO ₂	0.27	0.14	0.16	—	—	0.50	—	0.60	0.05
MnO ₂	—	—	—	—	—	0.02	—	—	—
P ₂ O ₅	0.03	—	—	—	—	0.03	—	—	0.02
CaO	0.09	0.15	0.06	0.08	0.07	1.06	0.17	0.17	0.14
MgO	4.33	4.43	6.56	1.68	2.31	3.88	2.40	2.25	0.13
Na ₂ O	2.92	2.80	3.87	1.95	3.06	2.16	2.79	2.56	2.80
K ₂ O	0.07	0.14	0.14	0.10	0.11	0.12	0.08	0.42	0.07
Ignition loss	20.80	16.11	14.10	17.90	12.66	15.62	—	12.27	14.40
Total	99.91	100.04	100.04	100.04	100.40	99.55	—	99.63	99.92
Na ₂ O	2.92	2.64	3.41	1.78	3.03	2.16	2.41	2.15	—
K ₂ O	0.07	0.10	0.09	0.07	0.13	0.12	0.06	0.09	—
CaO	0.09	0.15	0.05	0.08	0.07	1.06	—	0.08	—
MgO	—	0.18	0.23	0.13	0.07	0.10	—	0.03	—

¹ Expressed as percent metallic oxide

² Nontronite

Types of Dissolution Curves

In general, three types of acid-dissolution curves were obtained:

1. The straight-line curves of the Polkville, Mississippi, sample (Fig. 1) have already been described. The straight lines obtained from a semi-logarithmic plot show that the dissolution of iron, aluminum, and magnesium is a first-order reaction.
2. A second type of curve which becomes asymptotic with time is illustrated by the acid dissolution of aluminum from montmorillonite, Otay, California (Fig. 2, curve *A*). Subtraction of approximately 1.70 per-

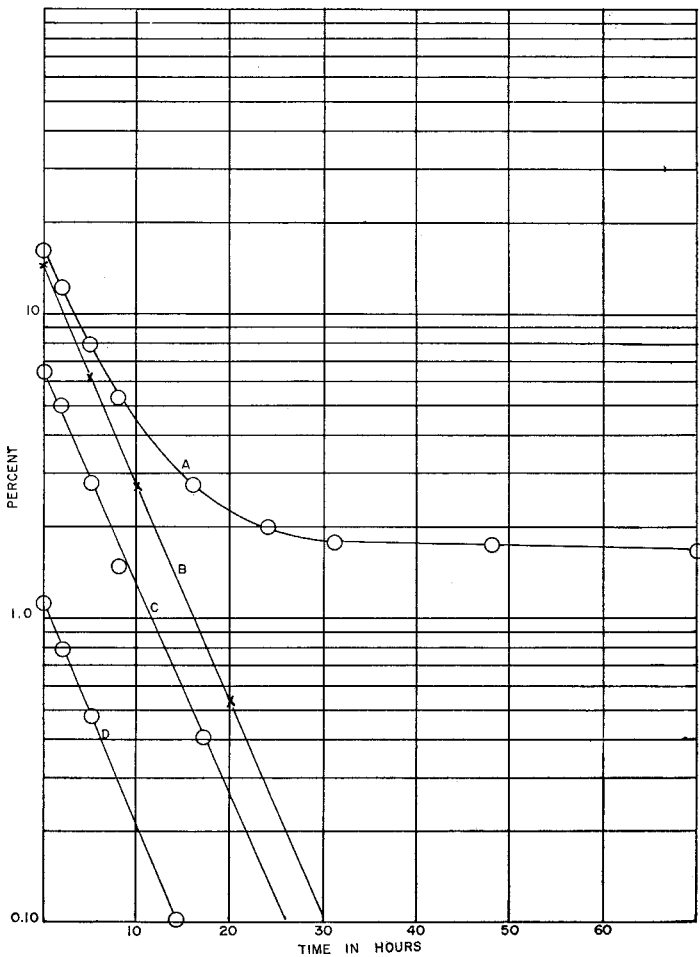


FIGURE 2.—Dissolution curves of montmorillonite, Otay, Calif. *A*, Total aluminum. *B*, Octahedral aluminum. *C*, Octahedral magnesium. *D*, Octahedral iron.

cent of extremely insoluble aluminum, expressed as the oxide, from curve *A* gives a straight line *B* having a slope similar to lines *C* and *D* which have been interpreted as octahedral magnesium and iron, respectively. By analogy line *B* represents the dissolution of octahedral aluminum. The straight lines obtained by this method of plotting show again that the dissolution of the three ions is first-order.

3. The third type of curve is shown by the dissolution of aluminum from montmorillonite, Clay Spur, Wyoming (Fig. 3). A decreasing curve is obtained which eventually becomes a straight line. Extrapolation of this straight-line portion to zero time, line *B*, gives the amount of tet-

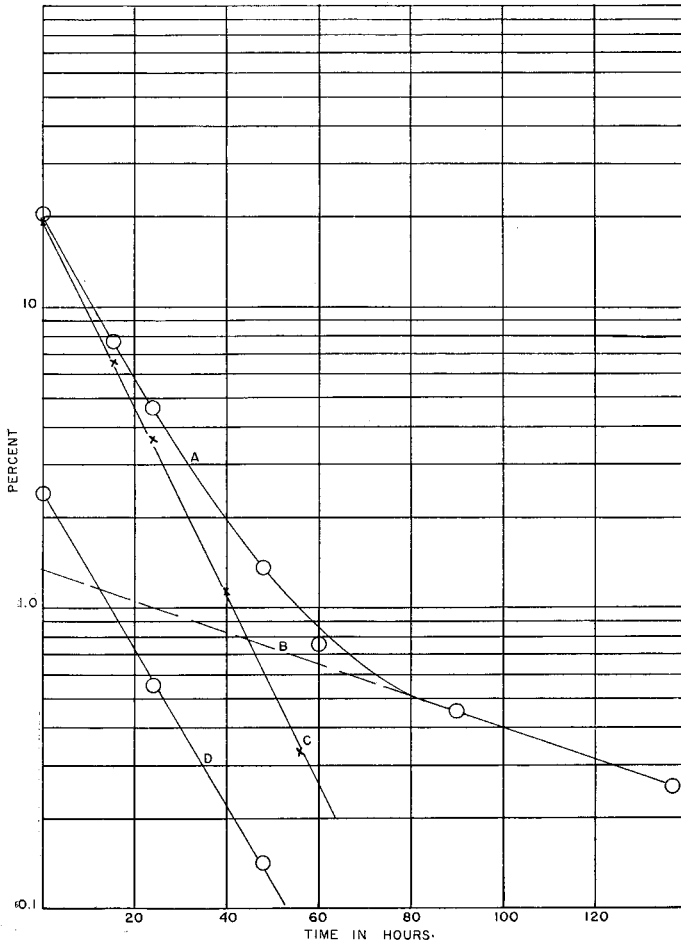


FIGURE 3.—Dissolution curves of aluminum and magnesium in montmorillonite, Clay Spur, Wyo. *A*, Total aluminum, *B*, Tetrahedral aluminum. *C*, Octahedral aluminum. *D*, Octahedral magnesium.

rahedral aluminum. Subtraction of line *B* from curve *A* gives a straight line, *C*, which has a slope similar to line *D*, the dissolution curve of octahedral magnesium. Therefore, it is interpreted that line *C* represents the dissolution of octahedral aluminum. The straight lines obtained for octahedral aluminum and magnesium and tetrahedral aluminum show that these ions are removed from their respective lattice positions as first-order reactions.

As it is impossible to include all of the dissolution curves of the eight montmorillonites in this paper, only those that illustrate an important point are shown (Figs. 1 to 7). However, Table 2 summarizes the distribution of iron, aluminum, magnesium, and titanium as interpreted from the respective acid-dissolution curves of the eight montmorillonite specimens.

Inspection of Table 2 shows that a fraction of the total iron present in four of the samples is either in tetrahedral coordination or as extraneous material.

Aluminum is found extraneous to the clay lattice in three samples and in tetrahedral coordination in all but three samples. The Amory, Mississippi, sample is conspicuous by the presence of three forms of aluminum: tetrahedral, octahedral, and extraneous (Fig. 4).

Titanium curves were established for only two samples because the small amount present in the other clays could not be measured accurately. Although the titanium curve for the Amory, Mississippi, sample has been interpreted as indicating titanium in octahedral coordination, it is possible that this metal ion is present as an impurity having the same solution rate as octahedral magnesium (Fig. 5). This, however, cannot be decided from the available data; to be consistent in the interpretation of the dissolution curves, titanium in the Amory sample is considered to be in octahedral coordination.

In contrast to the above mentioned titanium curve, the Plymouth, Utah, sample gives a titanium curve that shows no relation to the curves for the other octahedral ions of the clay lattice (Fig. 6). Therefore, titanium in this clay is considered to be present as an impurity.

Magnesium is the only ion in the samples which have been examined that always gives a straight-line dissolution curve. Since magnesium occurs in only octahedral coordination, except for a very small amount in the interlayer, the straight-line dissolution curves substantiate the theory that an ion in only one

TABLE 2.—DISTRIBUTION OF IRON, ALUMINUM, MAGNESIUM, AND TITANIUM INTERPRETED FROM THE RESPECTIVE DISSOLUTION CURVES OF EIGHT MONTMORILLONITES

Type specimen	Expressed as percent Fe ₂ O ₃			Expressed as percent Al ₂ O ₃			Expressed as percent MgO		Expressed as percent TiO ₂	
	Oct.	Tet.	Ex.	Oct.	Tet.	Ex.	Oct.	Ex.	Oct.	Ex.
Polkville, Miss.	1.05	—	0.53	16.40	—	—	4.33	—	—	—
Santa Rita, N. Mex.	1.02	—	—	16.10	—	1.05	4.25	—	—	—
Otay, Calif.	1.10	—	—	14.55	—	1.70	6.34	—	—	—
Merritt, B. C.	3.60	—	—	12.83	1.9	—	1.55	—	—	—
Amory, Miss.	2.60	—	4.2	13.20	0.8	5.2	2.22	—	0.6	—
Belle Fourche, S. Dak.	4.07	—	—	18.92	2.4	—	2.24	—	—	—
Plymouth, Utah	3.45	0.86	—	16.70	0.9	—	3.78	—	—	0.50
Clay Spur, Wyo.	3.37	0.33	—	18.90	1.4	—	2.40	—	—	—

Key: Oct. — Octahedral; Tet. — Tetrahedral; Ex. — Extraneous

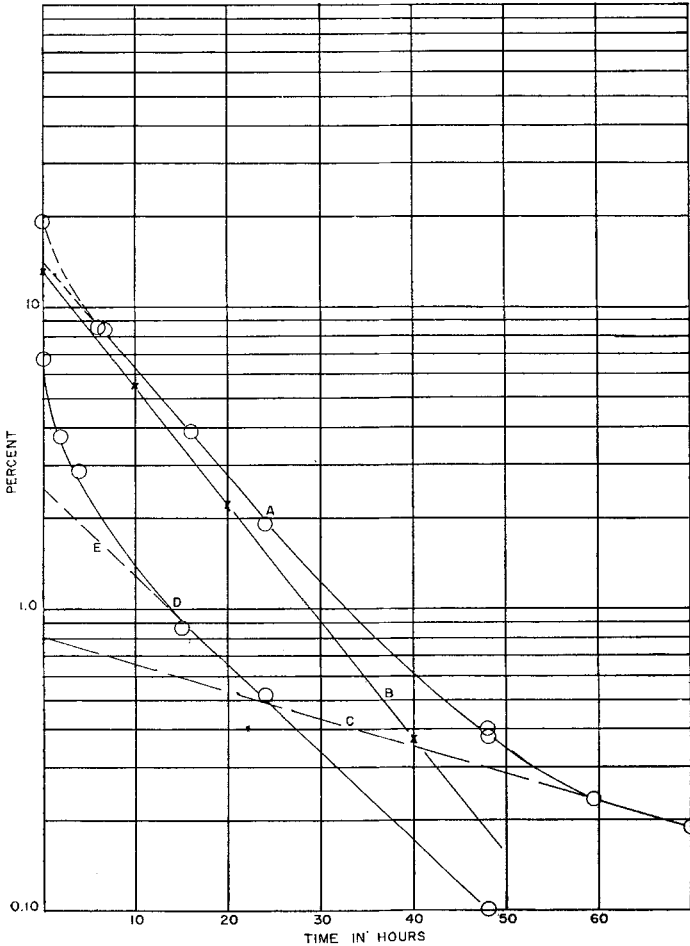


FIGURE 4.—Dissolution curves of aluminum and iron in montmorillonite, Amory, Miss. *A*, Total aluminum. *B*, Octahedral aluminum. *C*, Tetrahedral aluminum. *D*, Total iron. *E*, Octahedral iron.

coordination state gives a straight-line dissolution curve. Magnesium is also the only ion that does not occur as an impurity.

Acid-Dissolution Analysis

Acid-dissolution curves are presented that have been resolved in terms of the structure and composition, within experimental error. The technique of acid dissolution offers promise for a method of distinguishing between different coordination states of ions and of enabling the ions to be measured separately.

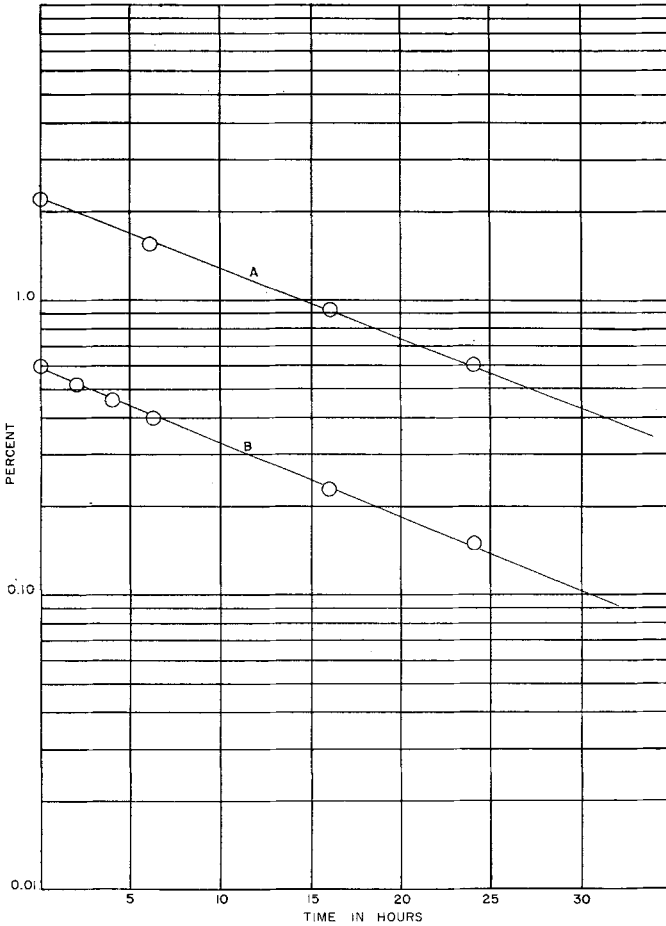


FIGURE 5.—Dissolution curves of magnesium and titanium in montmorillonite, Amory, Miss. *A*, Octahedral magnesium. *B*, Octahedral titanium.

Silicon, however, still remains as a difficulty. Foster (1953) has described a method of determining the amount of extraneous silicon or aluminum in montmorillonites. Essentially the method consists of comparing the ratios of silicon to aluminum before and after alkaline digestion. It is obvious that if both extraneous silicon and aluminum are present, the ratios will be in error. Foster (personal communication) stated that only one extraneous ion, silicon or aluminum, was assumed to be present as an impurity.

The presence of extraneous silica in some of these samples is indicated by the x-ray results of Earley, Osthaus, and Milne (1953) on samples prepared by a similar method from the same stock supply of bentonites. Fortunately structural silicon can be calculated and extraneous silicon determined by difference.

The method of calculation is based on the idealized Hofmann-Endell-Wilm structure of montmorillonite $[Al_4Si_8O_{20}(OH)_4]$ and on the following two assumptions: (a) The sum of the charges of all interlayer cations balances the charges on the tetrahedral and/or octahedral layers of the lattice. Hence, octahedral charge must be numerically equal to the difference between interlayer charge and tetrahedral charge. (b) The lattice unit contains eight tetrahedral positions, each of which must be occupied by some cation. Therefore, tetrahedral silicon is numerically equal to the difference between eight and the sum of tetrahedral aluminum and iron ions per lattice unit.

In samples which do not have tetrahedral substitution, the charge obviously originates exclusively on the octahedral layer. The dissolution data (Table 2) indicate that this is the case with the Otay, Polkville, and Santa Rita samples.

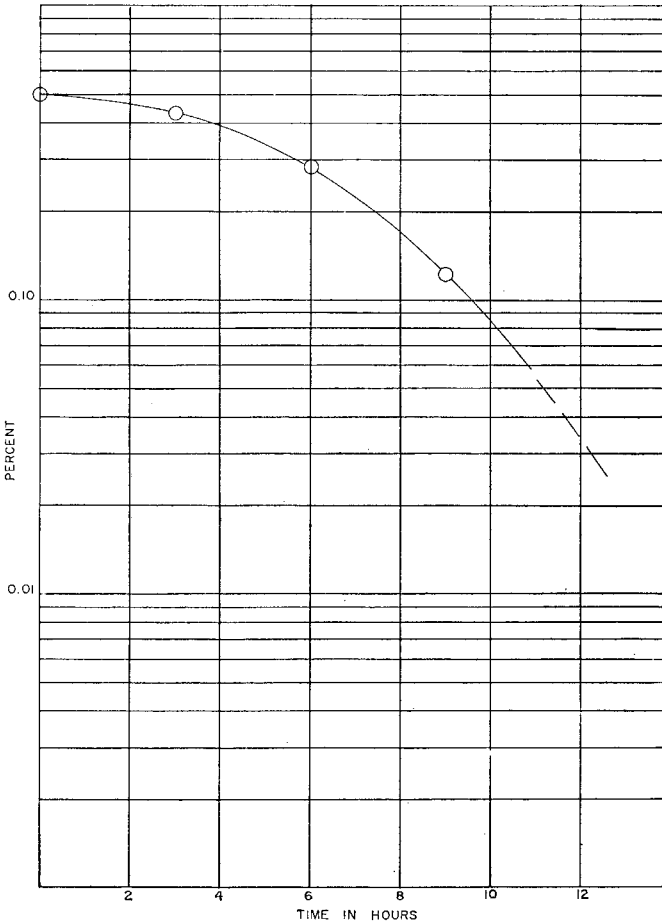


FIGURE 6.—Dissolution curve of extraneous titanium in montmorillonite, Plymouth, Utah.

Assuming the extrapolations reported in Table 2 to be accurate, the sum of the charges of all octahedral cations in these samples plus the charges of all interlayer cations must be exactly 12 per lattice unit. Therefore, the ratio of 12 to the sum of equivalents or charges of the octahedral and interlayer cations is the factor by which relative gram atoms are multiplied in order to convert relative gram atoms into atoms per lattice unit. Since there seems to be no tetrahedral substitution in these samples, the percent of silicon dioxide required to fill eight tetrahedra is readily calculated by dividing eight by the factor just referred to and then multiplying the quotient by the molecular weight of silicon dioxide (60.06). The details of the method are illustrated in Table 3.

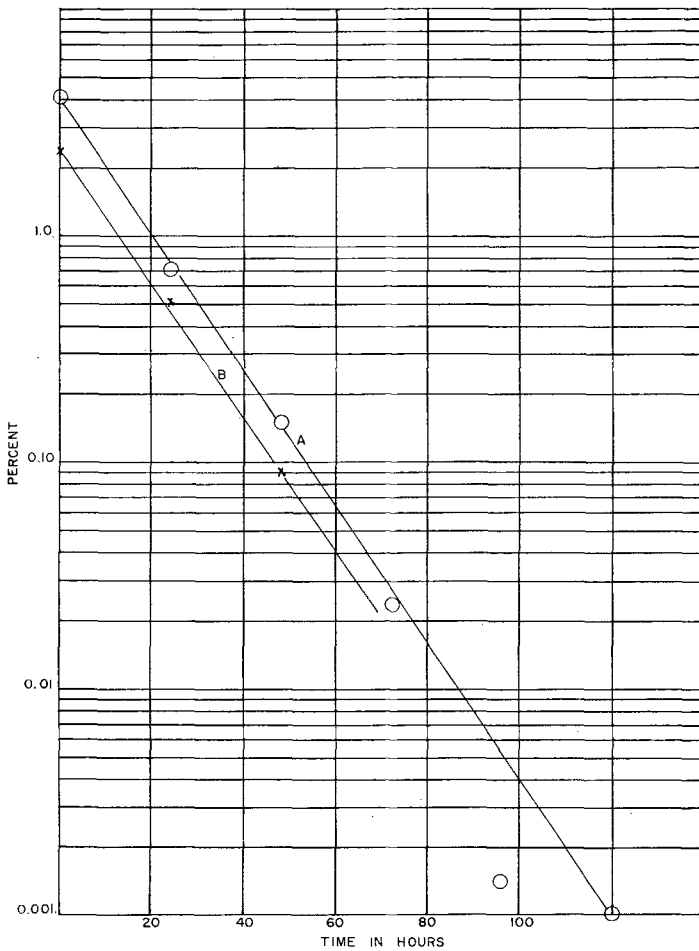


FIGURE 7.—Dissolution curves of iron and magnesium in montmorillonite, Belle Fourche, South Dakota. *A*, Octahedral iron. *B*, Octahedral magnesium.

TABLE 3.—OTAY MONTMORILLONITE. CALCULATION OF CATION DISTRIBUTION PER UNIT CELL ON THE BASIS OF ACID-DISSOLUTION DATA.

			Per 100 grams		Atoms per unit cell
Percent			Gram atoms	Equivalents or charges	
Octahedral	Al ₂ O ₃	14.55	Al .28546	0.85638	Tetra Si 8.000 (assumed)
"	Fe ₂ O ₃	1.10	Fe .01378	0.04133	
"	MgO	6.33	Mg .15699	0.31399	
Interlayer	Na ₂ O	3.41	Na .11001	0.11001	Octa { Al 2.562 Fe 0.124 Mg 1.409 ----- 4.09
"	K ₂ O	0.09	K .00191	0.00191	
"	CaO	0.05	Ca .00089	0.00178	
"	MgO	0.23	Mg .00570	0.01140	
				1.33680	
Factor = 12./1.3368 = 8.9766					Inter- layer { Na 0.987 K 0.017 Ca 0.008 Mg 0.051
Calculated SiO ₂ = 8.0/8.9766 × 60.06 = 53.52 percent					
SiO ₂ by analysis = 57.80 percent					
Extraneous SiO ₂ = 4.28 ¹ percent					

¹ Accuracy depends solely on the correctness of extrapolated Al₂O₃ (1.70 percent) and the accuracy of analysis.

The calculation is somewhat more complicated with samples which contain tetrahedral substitution, for in such samples the charge is not exclusively on the octahedral layer of the lattice. Nevertheless, the calculations can still be made. The method is similar to that outlined in the preceding paragraph, but instead of making use of the whole of the equivalents or charges of interlayer cations in calculating the factor, only that part is used which is required to balance the octahedral charge. This must be the difference between total interlayer charge and tetrahedral charge. Since one charge results from each tetrahedral substitution of aluminum and/or iron for silicon, the effective tetrahedral equivalent or charge is numerically the same as gram atoms of tetrahedral substitution. Subtracting this quantity from the sum of equivalents or charges of all interlayer cations gives equivalents or charges corresponding to the octahedral equivalent or charge. The ratio of 12 to the sum of the quantity thus found and equivalents or charges of all octahedral cations gives the factor by which all gram atoms are multiplied in order to convert them into atoms per lattice unit. The use of a common factor for converting all essential gram cations contained in a given sample into atoms per unit cell is essential because the ratios of all cations must be maintained throughout the calculation. An example of the calculation for samples with tetrahedral substitution is given in Table 4.

Table 5 reports the distribution of cations per unit cell, as calculated by the foregoing method. All the samples of montmorillonite used in this study appear to be substantially dioctahedral. In any case, the percentage of unit cells that are not dioctahedral is relatively small.

TABLE 4.—MERRITT MONTMORILLONITE. CALCULATION OF CATIONS PER UNIT CELL ON THE BASIS OF ACID-DISSOLUTION DATA.

			Per 100 grams		Cations per unit cell
Percent			Gram atoms	Equivalents or charges	
Tetrahedral	Al ₂ O ₃	1.90	Al	0.0373	Tetra { Si 7.555 ³ Al 0.445 ----- 8.00
Octahedral	Al ₂ O ₃	12.83	Al	0.2517	
"	Fe ₂ O ₃	3.60	Fe	0.0451	
"	MgO	1.55	Mg	0.0384	
Interlayer	Na ₂ O	1.78	Na	0.0574	Inter-layer { Na 0.690 K 0.018 Ca 0.017 Mg 0.038
"	K ₂ O	.07	K	0.0015	
"	CaO	.08	Ca	0.0014	
"	MgO	.13	Mg	0.0032	
					0.0308 ¹
					0.9980 ²

¹Total interlayer equivalents or charges = 0.0681
 Gram atoms tetrahedral Al = 0.0373
 Interlayer equivalent or charge corresponding to octahedral equivalent or charge = 0.0308
²Factor = 12.0/.998 = 12.024
³Calculated SiO₂ 7.555/12.024 × 60.06 = 37.62 percent
 SiO₂ found by analysis = 60.00 percent
 Extraneous SiO₂ = 22.28 percent

The method used for calculating atoms per lattice unit involves the assumptions that the analyses and extrapolations were accurate and that the Hofmann, Endell, and Wilm structure of montmorillonite is essentially correct. The results for the Amory sample were possibly influenced to some degree by the fact that this sample apparently contains small amounts of hydrous mica. This is indicated by the x-ray data reported by Earley, Osthaus, and Milne (1953) and by the fact that the sample contains significant amounts of nonexchangeable potassium. Therefore, it is possible that an unknown but probably small part of the exchangeable cations of this sample came from this kind of impurity. Also some unknown part of the acid-soluble aluminum and possibly iron may have been from hydrous mica. For these reasons both the calculations for this sample, as reported in Table 5, and the extrapolations shown in Figure 4 may be somewhat in error. The Amory sample is the only one reported herein for which evidence has been obtained of significant amounts of any silicate other than montmorillonite; with all the other samples the impurities seem to be in the form of amorphous or poorly crystallized material.

The fact that the Merritt sample was found to contain a relatively large percentage of extraneous silicon dioxide (Table 4) is consistent with the evidence obtained by Earley, Osthaus, and Milne (1953) who found that this montmoril-

lonite gave strong x-ray lines corresponding to cristobalite. Also the results of calculation on the basis of total analysis of this sample show considerably more than eight silicon atoms per unit and less than four total octahedral cations per unit. Results of this kind afford strong evidence of a substantial amount of extraneous silica in the sample.

The Otay sample is interesting for the reason that it affords an illustration of the effects of impurities on the calculated distribution of cations in the lattice. When the calculation is made on the basis of total analysis of this sample, the final results are not greatly different from those shown in Table 3 because the sample apparently contains both extraneous silica and extraneous alumina, the effects of which on the calculated results tend to cancel each other. Consequently, a rational lattice can be calculated for grossly impure samples.

It is noteworthy that the iron-bearing impurity in the Polkville sample is relatively soluble, while the aluminum-bearing impurity of the Otay sample is pronouncedly resistant to solution by hydrochloric acid.

The presence of small amounts of tetrahedral iron in the Plymouth and Clay Spur samples is especially noteworthy. This finding is consistent with the results on nontronite, as previously reported by the author (Osthaus, 1954). This appears to be the first time that tetrahedral iron has been reported as a constituent of bentonitic montmorillonite.

The calculations reported in Tables 3, 4, and 5 afford supporting evidence that the method of resolving the dissolution curves used in this study is basically sound.

In view of the fact that the samples used in this study had been subjected to purification by sedimentation and supercentrifugation, and that only extremely small particles were used (0.2 to 0.05 microns), it is possibly surprising that

TABLE 5. — DISTRIBUTION OF CATIONS PER LATTICE UNIT IN MONTMORILLONITE SAMPLES

		Otay, Calif.	Polkville, Miss.	Santa Rita, N. Mex.	Merritt, B.C.	Amory Miss.	Belle Fourche, S. Dak.	Clay Spur, Wyo.	Plymouth Utah
Tetrahedral	Si	8.000	8.000	8.000	7.552	7.823	7.607	7.731	7.754
	Al	—	—	—	0.448	0.177	0.393	0.234	0.153
	Fe	—	—	—	—	—	—	0.035	0.093
		8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Octahedral	Al	2.562	2.929	2.920	3.026	2.915	3.100	3.166	2.837
	Fe	0.124	0.119	0.118	0.542	0.362	0.426	0.360	0.374
	Mg	1.409	0.977	0.974	0.462	0.620	0.464	0.508	0.812
	Ti	—	—	—	—	0.085	—	—	—
		4.09	4.02	4.01	4.03	3.98	3.99	4.03	4.02
Interlayer	Na	0.987	0.857	0.787	0.690	0.781	0.816	0.664	0.603
	K	0.017	0.014	0.019	0.018	0.021	0.023	0.011	0.022
	Ca	0.008	0.015	0.025	0.017	0.016	0.010	—	0.164
	Mg	0.051	—	0.041	0.039	0.008	0.014	—	0.021
Determined	SiO ₂ *	57.80	53.42	58.10	60.00	55.39	56.80	54.90	54.25
Calculated	SiO ₂ *	53.52	52.78	51.98	37.72	41.74	54.71	54.38	53.78
Extraneous	SiO ₂ *	4.28	0.64	6.12	22.28	13.65	2.09	0.52	0.47

* Percent

certain samples were found to contain so much impurity, amounting to as much as 22.28 percent in the Merritt sample. The results emphasize the fact that formulas for bentonitic montmorillonites calculated on the basis of total chemical analysis are not likely to be highly accurate.

Factors Influencing Acid-Dissolution

The author (Osthaus, 1954) showed that a semilogarithmic plot of the undissolved iron, aluminum and magnesium against time was a straight line or a curve that could be resolved into two straight lines. By definition the straight line in such a plot represents a first-order reaction. The rate equation of a first-order reaction states that the reaction rate is proportional to the quantity of unchanged product as shown in equation 1

$$\frac{dM}{dt} = -k M \text{ equation 1}$$

where *M* is the concentration of undissolved metal ion, *t* the time and, *k* the rate constant. Integration of equation 1 between the limits of zero time when the concentration of metal is *M*₀ and time *t* yields

$$\ln M = \ln M_0 - kt \text{ equation 2}$$

In the form of the logarithm to the base 10, equation 2 gives

$$\log_{10}M = \log_{10}M_0 - \frac{k}{2.3} t \text{ equation 3}$$

Thus the rate constant is 2.3 times the slope of the straight line in the semilogarithmic plot.

In the early work, dissolution studies were made at constant acid concentration and temperature. Sufficient acid must be present during the digestion that its consumption during the clay-acid reaction has a negligible effect on the acid concentration in the flask. Thus, in a given experiment the acid concentration may be considered as a constant. Several of the acid-dissolution curves were established by digesting half-gram samples of clay in 100 ml of ten percent by volume hydrochloric acid. This ratio of acid to clay exceeds the theoretical amount required to dissolve iron, aluminum, and magnesium by at least a factor of ten. However, it was found that the rate constant would increase if the acid concentration was increased. Figure 8 shows a threefold increase in the slope of the straight lines, *A* and *C*, as the acid concentration is increased from 10 to 30 percent hydrochloric acid.

This indicates that the reaction is also first-order with respect to acid concentration. Equation 1 can be revised to give

$$\frac{dM}{dt} = -k^* A M \text{ equation 4}$$

where *A* is the acid concentration and *M* the concentration of the metal ion.

However, in a single dissolution study the acid concentration remains constant and thus can be included in the measured rate constant *k* shown in equation 5.

$$k = k^* A \text{ equation 5}$$

The true rate constant k^* , which must be independent of acid concentration as well as concentration of undissolved metal, is then the apparent rate constant divided by the acid concentration.

The effect of temperature was studied on the dissolution of montmorillonite, Polkville, Mississippi. The first dissolution curve of this clay indicated two forms of iron, octahedral and extraneous (Fig. 1). Figure 9 shows that curves C and D (the dissolution of octahedral iron at two different temperatures) have the same intersection at zero time within experimental error. If the rate constants

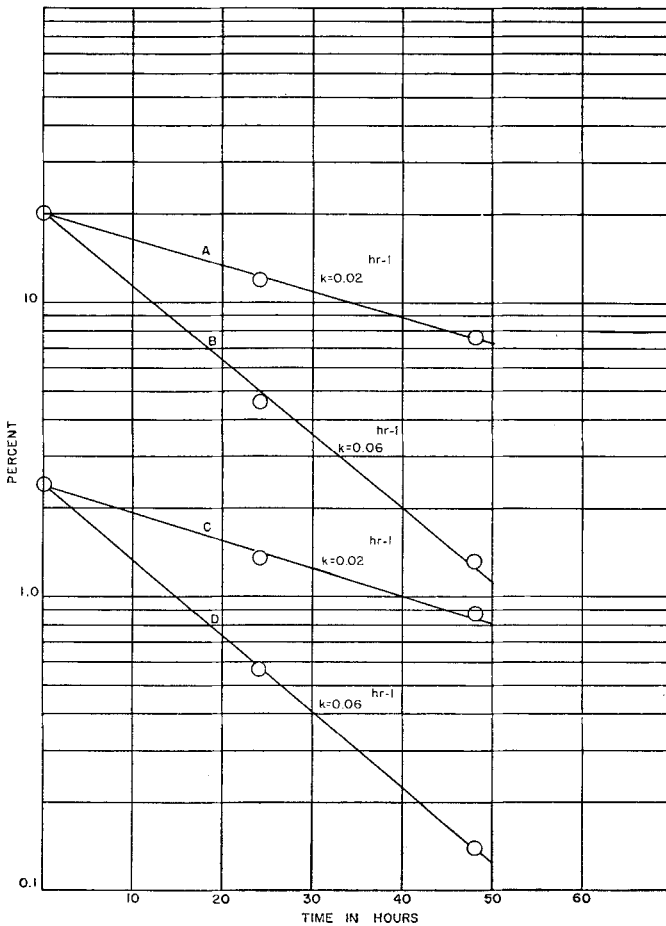


FIGURE 8.—Dissolution curves of aluminum and magnesium in 10 and 30 percent by volume hydrochloric acid, montmorillonite, Clay Spur, Wyo. A, Aluminum 10 percent acid. B, Aluminum 30 percent acid. C, Magnesium 10 percent acid. D, Magnesium 30 percent acid.

(*k*) are calculated by use of equation 3 for the octahedral iron represented by curves *C* and *D*, it is observed that the rate constant (*k*) approximately doubles for a ten-degree increase in temperature. Curves *E* and *F* are shown as broken lines, as they were determined from single digestions. If the rate constants (*k*) are calculated from the two respective slopes, a similar increase with temperature is observed. The effect of temperature upon the reaction rate constants will be considered in detail in the following section which deals with activation energies. Curves *A* and *B* indicate that at their respective temperatures the extraneous iron is not differentiated from the octahedral iron of the clay lattice.

The effect of temperature on the dissolution rate of octahedral aluminum was similar to the experimental results obtained for octahedral iron. Table 6 shows

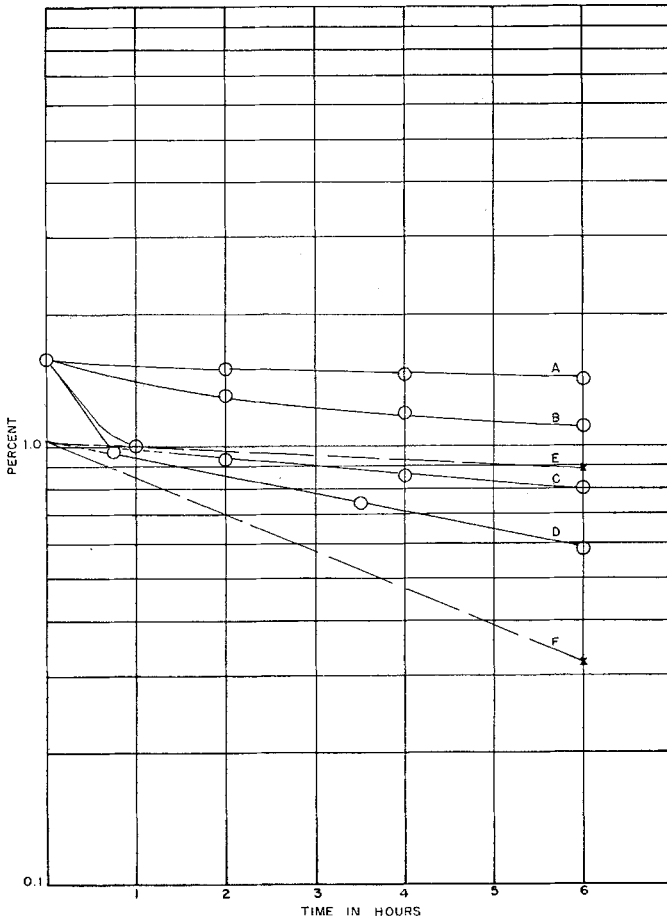


FIGURE 9.—Dissolution curves at different temperatures of iron in montmorillonite, Polkville, Miss. *A*, 32.2° C. *B*, 53.8° C. *C*, 83.5° C. *D*, 93° C. *E*, 72.0° C. *F*, 104° C.

the relation between the rate constants (k) of iron and aluminum and the temperature of digestion. It has been shown that the dissolution of the ions from the clay lattice is first-order over the range of acid concentration and temperature studied.

TABLE 6.—RATE CONSTANTS OF OCTAHEDRAL IRON AND ALUMINUM
MONTMORILLONITE, POLKVILLE, MISS.

Degrees C	31.0	49.0	53.8	72.3	83.5	93.0	95.2	104.0
Aluminum k , hr ⁻¹	0.002	0.005	0.005	0.022	0.040	0.095	0.099	0.185
Iron k , hr ⁻¹	—	—	—	0.022	0.040	0.099	—	0.198

If montmorillonites and nontronites are completely expandable, thereby permitting acid to react with all the iron, aluminum and magnesium ions statistically, the dissolution of a completely expandable mineral in acid can be considered as essentially analogous to a liquid-liquid reaction. Thus, hydrogen would be available to replace any of the metal ions of a given coordination with equal ease. This view is supported by the fact that an increase in temperature which increases ion mobility and an increase in acid concentration which increases the number of available ions speeds up the reaction proportionately in each case. In the cases of montmorillonite and nontronite it suggests that the metal ions can migrate through the edges and particularly the surfaces of the clay platelets and that the solid-liquid boundary has little or no differential effect on the transfer of ions. However, if the clays are not expandable or only partially expandable the transfer of metal ions may take place only at the edges of platelets. In this case the migration of ions would be affected by the rate of diffusion through the crystal structure. Thus, although acid-dissolution of montmorillonite and nontronite is a first-order reaction, it does not follow that acid-dissolution of nonexpandable clays will be first-order.

Activation Energies

The apparent activation energies have been determined for the solution of octahedral iron and aluminum in montmorillonite, Polkville, Mississippi, and octahedral and tetrahedral iron and aluminum in nontronite, Garfield, Washington.

The mean rate constants at two or more different temperatures were used in determining the activation energy since it is permissible to use the mean rate constants (k) instead of the true rate constant (k^*) for the calculation of activation energies as long as all the dissolution experiments are made with the same concentration of acid.

A quantitative relationship is given by the Arrhenius equation

$$k = Ae^{-E/RT} \text{ equation 6}$$

- where k = specific rate constant (hour⁻¹)
 A = constant
 E = activation energy in calories per mole
 R = gas constant, Cal.₁₅ · Deg.⁻¹ · mole⁻¹
 T = absolute temperature

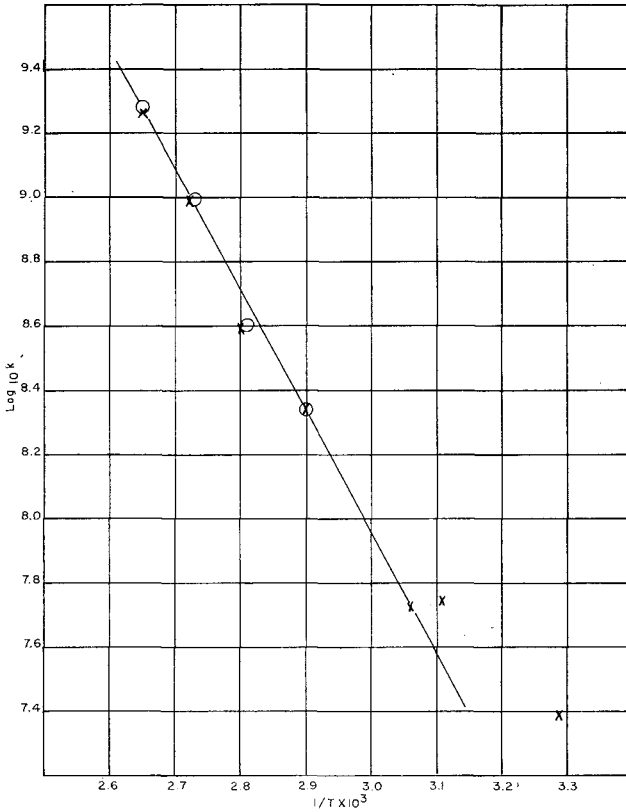


FIGURE 10.—Logarithms of the rate constants (*k*) of octahedral iron and aluminum in montmorillonite, Polkville, Miss., plotted against the reciprocal of the absolute temperature; X, Octahedral aluminum, and O, Octahedral iron.

The logarithmic expression of equation 6 is

$$\text{Log}_{10}k = -\frac{E}{2.303R} (1/T) + C \text{ equation 7}$$

A straight line should result from a plot of $\text{Log}_{10}k$ against $1/T$, with a negative slope of $-E/2.303R$.

If the experiments are repeated at a different acid concentration a different set of rate constants will be obtained which differ from the original values by a constant factor. Thus, in the logarithmic plot another straight line will be obtained which is parallel to the first and thus yields the same activation energy. For a comparison of activation energies of various clays, the determinations may be made at a convenient acid concentration since the acid concentration will not affect the value obtained for the activation energy.

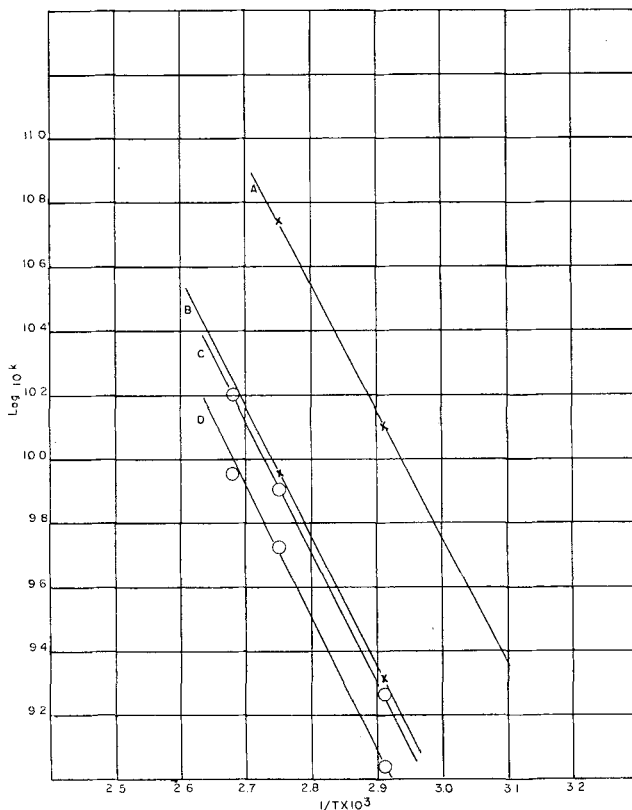


FIGURE 11.—Logarithms of the rate constants (k) of octahedral and tetrahedral iron and aluminum in nontronite, Garfield, Wash., plotted against the reciprocal of the absolute temperature. *A*, Octahedral aluminum. *B*, Tetrahedral aluminum. *C*, Octahedral iron. *D*, Tetrahedral iron.

The logarithms of the rate constants (k) of octahedral iron and aluminum for montmorillonite from Polkville, Mississippi, shown in Table 6 were plotted against the reciprocals of the respective absolute temperatures (Fig. 10). The plotted values of iron and aluminum fall on approximately the same line, and within experimental error. The apparent activation energy for each ion amounts to 17 kilocalories per mole.

Iron dissolution curves for nontronite from Garfield, Washington, were established at 71°, 91°, and 101.5° C and were resolved into octahedral and tetrahedral components for which the rate constants (k) were calculated for the respective temperatures. Acid-dissolution curves were established at 71° and 91° C for aluminum and were resolved into octahedral and tetrahedral components, and the rate constants (k) calculated. These rate constants are plotted against the reciprocal of the observed absolute temperature in Figure 11. The

four slopes of the octahedral and tetrahedral iron and aluminum curves are identical within experimental error, and yield an activation energy of 18 kilocalories per mole.

CONCLUSIONS

Acid-dissolution of aluminum, iron and magnesium from eight montmorillonites and a nontronite takes place as a first-order reaction with respect to temperature and acid concentration over the ranges that were investigated. The amounts of the metal ions in tetrahedral and in octahedral coordination in the clay lattice can be determined experimentally except for silicon which can be calculated using the dissolution data. In addition the presence of extraneous aluminum- and iron-bearing impurities can be detected in many samples.

The rate constants for the dissolution reactions are nearly the same for aluminum, iron, and magnesium in octahedral coordination. Similarly the rate constants for aluminum and iron in tetrahedral coordination are nearly the same. However, the rate constants for ions in octahedral coordination are significantly different from those in tetrahedral coordination. Further, the rate constants vary considerably between samples. An increase in the temperature of digestion or in acid concentration results in a proportional increase in rate constants.

Activation energies were determined for the solution of iron and aluminum from a montmorillonite and a nontronite. The values obtained, 17-18 kilocalories per mole, were the same for both samples and for octahedral and tetrahedral ions.

ACKNOWLEDGMENTS

The author is indebted to the following: Dr. W. P. Kelley for the method of calculating lattice silicon; Dr. J. R. Tomlinson for the discussion of the chemical kinetics of acid-dissolution; and Dr. J. W. Earley for his guidance and supervision in the preparation of this report.

REFERENCES

- Brindley, G. W., and Youell, R. F., 1951, A chemical determination of the tetrahedral and octahedral aluminum ions in a silicate: *Acta Cryst.*, v. 4, p. 495-497.
- Earley, J. W., Osthaus, B. B., and Milne, I. H., 1953, Purification and properties of montmorillonite: *Amer. Min.*, v. 38, p. 707-724.
- Foster, M. D., 1953, Geochemical studies of clay minerals: III The determination of free silica and free alumina in montmorillonites: *Geochimica et Cosmochimica Acta*, v. 3, p. 143-154.
- Karsulin, M., and Stubican, Vl., 1954, Über die Struktur und die Eigenschaften synthetischer Montmorillonite: *Monatshefte für Chemie*, v. 85, p. 343-358.
- Kelley, W. P., 1945, Calculating formulas for fine grained minerals on the basis of chemical analysis: *Amer. Min.*, v. 30, p. 1-26.
- Kerr, P. F., and others, 1951, Reference clay minerals: A.P.I. Project 49.
- Osthaus, B. B., 1954, Chemical determination of tetrahedral ions in nontronite and montmorillonite: in *Clays and clay minerals*, Nat. Acad. Sci.—Nat. Res. Council, Pub. 327, p. 404-417.
- Ross, C. S., and Hendricks, S. B., 1945, Minerals of the montmorillonite group, their origin and relation to soils and clays: U. S. Geol. Survey Prof. Paper 205-B, p. 23-79.