REACTIONS OF FELDSPAR AND MICA WITH WATER AT LOW TEMPERATURE AND PRESSURE[1]
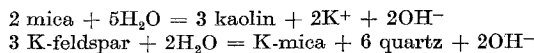
by

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ABSTRACT

Muscovite and K-feldspar (adularia) were dry-ground to -200/inch particles, which were suspended in water. These suspensions were " titrated " with KCl, and the pH was recorded as a function of KCl concentration and temperature. The results indicate that muscovite and adularia react with water to produce a surface film in which H^+ has displaced K^+. The " titration " curves show some characteristics attributable to exchange reactions, others apparently related to equilibria among solids of fixed composition. Maximum release of K^+ from adularia by reaction with water is much greater than that from mica. The interpretation is made that the first result of reaction of mica and adularia with water is a surface layer that grades from an outer portion that is structurally disrupted to an inner portion that retains the original silicate structure but with H^+ substituted for K^+. Addition of K^+ as KCl to the suspending solution displaces H^+ from the disrupted zone, but all H^+ originally taken up by the solids was not returned to the solution by concentrations of KCl up to 1.0 M. Experiments were of a few hours duration; work by others has shown that the disrupted zone releases appreciable concentrations of silica and alumina to solution over longer time intervals.

These hydrolysis experiments indicate that at 25°C an H-feldspar or H-mica structure is favored over a K-feldspar or K-mica structure except in solutions in which the ratio of a_{K^+}/a_{H^+} exceeds 10^{9-10} or 10^{7-8} respectively. These ratios decrease in the temperature range 25–65°C by a factor of about $10^{0.7}$. These results, where considered in relation to the observed behavior of feldspar and mica under weathering conditions, indicate that the major energy change for the reactions,

$$2 \text{ mica} + 5H_2O = 3 \text{ kaolin} + 2K^+ + 2OH^-$$
$$3 \text{ K-feldspar} + 2H_2O = \text{K-mica} + 6 \text{ quartz} + 2OH^-$$

can be considered to result from H^+–K^+ exchange, and that the energy contribution from other changes is small.
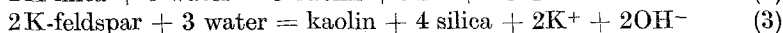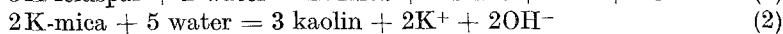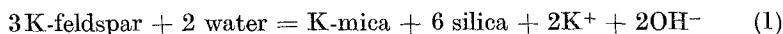
INTRODUCTION

During a recent graduate seminar in geochemistry at Harvard University, an attempt was made to summarize some of the excellent work of the past decade on hydrothermal alteration associated with veins. Because the zonal pattern of alteration of felsic rocks under moderate conditions of temperature and pressure is so uniform from place to place (cf. Sales and Meyer, 1950; Lovering, 1950; Schwartz, 1955), pointing to the effects of a common constituent of vein fluids, it was decided to investigate alteration reactions on

the simplest possible basis—an interaction of wall rocks with water. This decision was influenced strongly also by the striking results achieved by Morey and Chen (1955) using water leaches at relatively low temperatures and pressures.
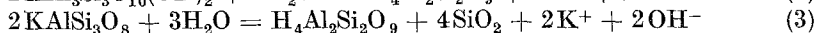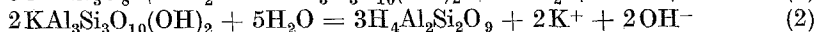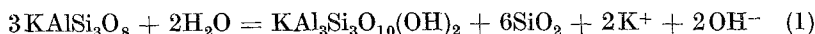
Chemical Reactions and Equilibria Relating
K-feldspar, K-mica and Kaolin

If attention is restricted to potassium feldspar, potassium mica and kaolin as important representatives of the much more varied alteration suite, one can write:

$$3\,\text{K-feldspar} + 2\,\text{water} = \text{K-mica} + 6\,\text{silica} + 2\text{K}^+ + 2\text{OH}^- \quad (1)$$
$$2\,\text{K-mica} + 5\,\text{water} = 3\,\text{kaolin} + 2\text{K}^+ + 2\text{OH}^- \quad (2)$$
$$2\,\text{K-feldspar} + 3\,\text{water} = \text{kaolin} + 4\,\text{silica} + 2\text{K}^+ + 2\text{OH}^- \quad (3)$$

Equation (3) is superfluous, in the sense that it is the sum of equations (1) and (2). That is, if the system is to have fields of stability of K-feldspar, K-mica and kaolin, K-mica appears as an intermediate product in the reaction sequence from feldspar to kaolin. The interrelations of the three equations are clarified by obtaining the equilibrium constants and then making plots of the variables involved.

At any given temperature and pressure the only variables are K^+ and OH^-, assuming that water is in excess and that the amount of dissolved K^+ and OH^- (or other dissolved species) is not sufficient to change the activity of water appreciably from unity. This appears from a derivation of the equilibrium constants:

$$3\,\text{KAlSi}_3\text{O}_8 + 2\text{H}_2\text{O} = \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 6\text{SiO}_2 + 2\text{K}^+ + 2\text{OH}^- \quad (1)$$
$$2\,\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 5\text{H}_2\text{O} = 3\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + 2\text{K}^+ + 2\text{OH}^- \quad (2)$$
$$2\,\text{KAlSi}_3\text{O}_8 + 3\text{H}_2\text{O} = \text{H}_4\text{Al}_2\text{Si}_2\text{O}_9 + 4\text{SiO}_2 + 2\text{K}^+ + 2\text{OH}^- \quad (3)$$

Because the activities of the solids and of water are unity, the equilibrium constants are all of the same form.

$$[\text{K}^+]^2\,[\text{OH}^-]^2 = k_{\text{feldspar-mica}} \quad (1)$$
$$[\text{K}^+]^2\,[\text{OH}^-]^2 = k_{\text{mica-kaolin}} \quad (2)$$
$$[\text{K}^+]^2\,[\text{OH}^-]^2 = k_{\text{feldspar-kaolin}} \quad (3)$$

Consequently, a plot of log K^+ versus log OH^- for a given temperature and pressure will produce parallel straight lines with a slope of -45 degrees. The relative positions of the lines representing the equilibria, on the assumption that all these minerals have stability fields, are shown in Fig. 1.

There are alternatives to this interpretation, but none seem as reasonable in terms of observed mineral relations. For example, if the reaction of K-feldspar to kaolin is not metastable, K-mica does not have a stability field, a conclusion refuted by the common K-mica–K-feldspar association in rocks.

Qualitative Effect of Temperature and Pressure

The positions of the equilibrium lines on the log K^+–log OH^- diagram can be estimated crudely from the following considerations. From the broad relation that feldspars are unstable in soils, and micas generally so, it can be concluded that the boundary lines lie at fairly high OH^- concentrations (pH $\geqslant$ 9) at surface temperatures and pressures. The abundance of mica and kaolin in hydrothermal alteration zones at moderate temperatures and pressures and of feldspar at high temperature and pressure, together with the
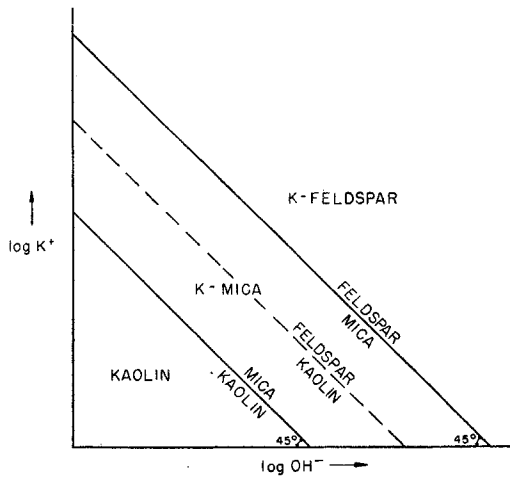

FIGURE 1.—Stability fields of K-feldspar, K-mica and kaolin as functions of K^+ and OH^- at an arbitrary temperature and pressure. The dashed line indicated the K-feldspar–kaolin reaction is metastable.

disappearance of kaolin, show that with increasing temperature and pressure the boundary lines probably trend toward a region of lower pH. Thus, a qualitative 3-dimensional diagram can be erected (Fig. 2).

On the basis of these general theoretical relations, it was decided to investigate the reactions of feldspar and mica with water at low temperature. Complete reconstitution of these minerals is known to be sluggish at low temperatures, but a first step might be the determination of the relative strength of the bonding of H^+ and K^+ in the feldspar and mica structures. Also, hydrolysis reactions at room temperature conceivably might provide a rough guide to the true kaolin–mica–feldspar equilibria.

ACKNOWLEDGMENTS

We are indebted to many people for suggestions and guidance in this work. The problem originally was developed in a geochemistry seminar at

Harvard University, and we have discussed various aspects with many of our colleagues in the geologic profession. Our greatest obligations, perhaps, are to Professor C. E. Marshall of the University of Missouri, to Professors Isaac Barshad, K. L. Babcock and Charles Meyer, and to Julian Hemley, all of the University of California. Dr Marshall read the original manuscript and made many valuable suggestions ; in addition, he made available to use at an early date his work with V. E. Nash that is cited in the bibliography. The physical picture of the surface reactions as proposed by Marshall and Nash has been a major factor in aiding our interpretation of our hydrolysis data.
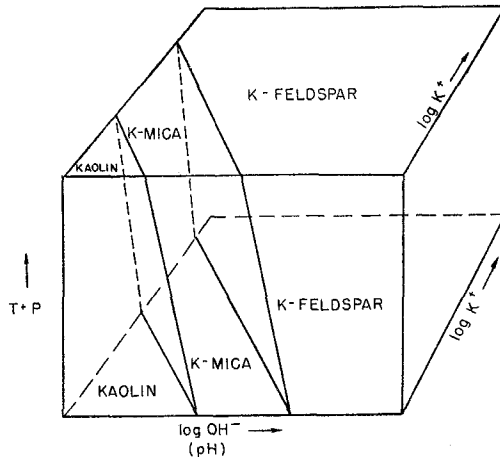

FIGURE 2.—Diagram showing general trend of kaolin, K-mica and K-feldspar equilibrium boundaries as functions of pH, log K^+, and increasing temperature and pressure of the environment.

Drs Barshad and Babcock also read the manuscript, and we hope that we have done justice to their many suggestions in clarifying material originally unclear or ambiguous. Through the course of the work, we have kept in active correspondence with Mr Hemley, who is working on high temperature–high pressure equilibria among feldspar, mica, kaolin and related alteration products under the direction of Dr Meyer, and we have traded ideas and information with him continuously.

PREVIOUS WORK

The reactions of feldspar and micas with water at low temperature and pressure have been studied by many workers. Of those studies especially pertinent to the present one, Tamm (1930) showed that suspensions of microcline in CO_2-free water can produce pH values as high as 10.7, if large amounts

of fine-grained feldspar are used. He titrated the suspensions alternately with HCl and KOH, and found that the reactions are essentially reversible. Also, he determined the sodium and potassium released to the water. Figure 3 is a plot derived from his data showing the concentration of bases released
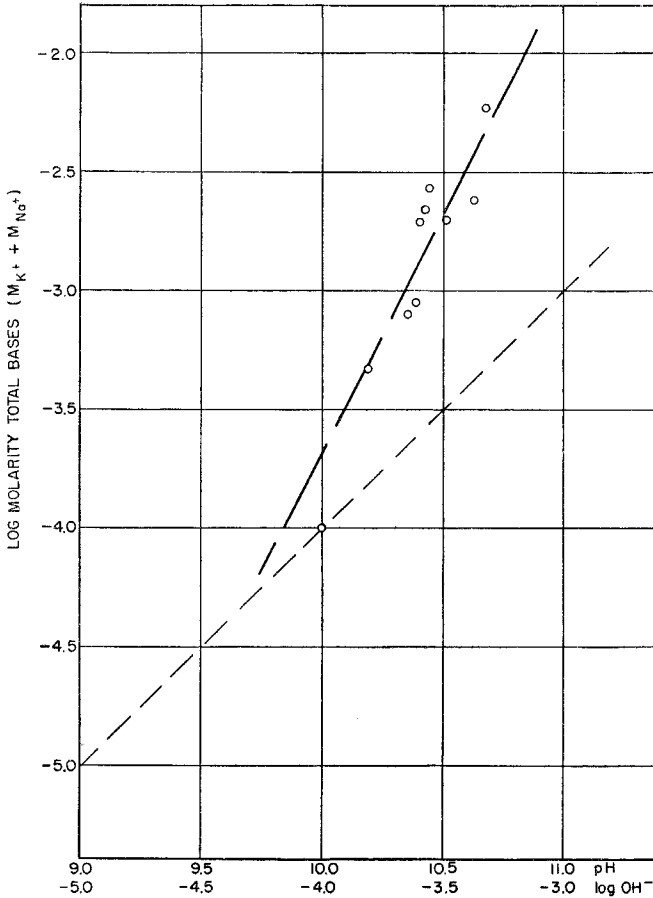
Figure 3.—Tamm's (1930) data on K + Na released to solution versus pH for suspensions of fine-grained microcline in air-free water. Short dashes show theoretical line if one OH⁻ is released for every K⁺ or Na⁺.

as a function of pH and log OH^+. The large excess of K^+ ($+Na^+$) over OH^- indicates that some negatively charged ionic species or surface must be present in the more concentrated suspensions to balance this excess K^+. The slope of the line that best fits his data shows a relation $\log K^+ = 2 \log OH^- + k$.

Correns and Von Engelhardt (1938) made a somewhat similar study of adularia except that in some experiments they controlled the pH of their suspensions, and also subjected the feldspar to a continuous supply of water or other reagent. They dialyzed the suspensions and showed that silica, alumina and potassium in ionic form are continuously released to a renewed water supply. Furthermore, their work showed that the atomic ratios of K/Si/Al released to pure circulated water over a period of weeks from a suspension of 1μ particles are of the order of 10.4/3.6/1, as opposed to the ratios in adularia of 1/3/1. In one experiment adularia was ground in a ball mill, the suspending water was passed through an ultrafilter, fresh water was added, and the operation repeated many times. The overall ratio of K/Si/Al released to solution was 46.3/1.89/1. Their work shows that: (1) In an open aqueous system, K, Si and Al are released into true ionic solution, but in ratios that leave a protective layer of hydrous aluminum silicate at the feldspar surface. (2) The specific values of the ratio K/Si/Al differ from those in pure water if pH is controlled by suitable reagents. (3) In the ball mill experiment, which most closely resembles our conditions because of its short duration, the ratio of released K to Si or Al is very high.

Armstrong (1940) ground feldspar in water and electro-dialyzed the suspension. His results also show that the constituents are released in ionic form, and that K^+ and Na^+ are by far the most abundant species in solution.

None of the investigators has been able to determine any crystalline phase in the feldspar alteration products.

Mitra and Rajagopalan (1948) suspended ground mica in water after converting it to the H^+-form, and titrated the mixture with KOH. Their curves show typical ion exchange behavior ; the titrations are reversible. Potassium ion was released to the solution.

In summary, both K-feldspar and K-mica react rapidly with water to give an alkaline solution, and the amount of K^+ freed is a function of the total surface exposed, as is the OH^- concentration achieved, suggesting that the water reacts to form at the feldspar or mica surface an insoluble H–Al–silicate which temporarily prevents further reaction. However, this H–Al–silicate, which can be visualized simply as an H-feldspar or H-mica, is not stable and breaks down in time to release silica and alumina, at least part of which is in true ionic solution. The dependence of the Al/Si ratio of ionically dissolved material on pH, demonstrated by Correns and Von Engelhardt (1938), probably is a measure of the solubility of the decomposition products ; but their calculation of the composition of the residual film on the mineral surface gives us little information concerning the possible phases. Orthoclase conceivably might, in time, develop a film of mica or silica or other solids at grain surfaces ; the composition of the solution in equilibrium with these solids could change with pH without necessarily removing these phases, or the phases could change composition.

Our interest was to determine the nature of the essentially instantaneous K^+–H^+ reactions. To this end, we reacted ground feldspar and mica with water, and then " back titrated " by adding KCl to the system.

EXPERIMENTAL

Materials Used

The feldspar used was an adularia. A nearly transparent single crystal was coarsely crushed, and fresh clean fragments were hand-picked to avoid a small amount of intergrown quartz and some unidentified surface contamination. No analysis of the particular specimen used is available, but the average composition of other samples from the same locality is given in Table 1. The hand-picked material was ground dry by a mechanically driven agate mortar and pestle until it passed through a 200-mesh inch screen. No other attempts were made to control grain size. The ground material was stored in stoppered glass jars and was used, in almost all experiments, within a day or two of grinding.

The mica used was part of a large single crystal of muscovite; the analysis is given in Table 1. Most of the mica was prepared in the same way as the feldspar; some was " ground " by shaving with a razor blade.

Table 1.—Analyses of Feldspar and Mica

	Adularia[1]	Muscovite[2]
SiO_2	65.2	45.87
Al_2O_3	19.0	38.69
Fe_2O_3	0.0	—
FeO	0.0	—
MgO	—	0.10
CaO	—	—
Na_2O	2.1	0.64
K_2O	13.8	10.08
H_2O	0.0	4.67
TiO_2	—	—
Total	100.1	100.05

[1] From Monte Fibbia, Gothard, Switzerland, Harvard University Mineralogy Museum Spec. no. 87356. Analysis averaged from those listed in Niggli, P., Koenigsberger, J. and Parker, R. L. (1940) *Die Mineralien der Schweizeralpen*, v. 2, p. 545.

[2] From Blue Mountain, Methuen Township, Ontario, Canada. Analysis from Hurlbut, C. S. (1956) Muscovite from Methuen Township, Ontario : *Amer. Min.*, v. 41, pp. 892–898.

Water was first passed through a commercial ion exchanger, then distilled in Pyrex glass from permanganate solution. After removal of air with pre-purified nitrogen, the pH of the water was 6.9–7.0.

Potassium chloride used was either reagent grade crystals or a saturated solution made with de-ionized and distilled water.

Experimental Procedure

In most experiments 200 ml of water was placed in duplicate reaction vessels and deaerated before addition of weighed ground feldspar or mica.

The pH was measured by means of a glass electrode and a saturated calomel electrode in each container; each container also was equipped with a temperature compensator and a solution ground. An amplifier and continuous recorder arrangement permitted alternate reading of the duplicate electrode pairs every eight seconds. Before and after each run, the electrodes were standardized with a pH-7 and a pH-4 buffer; there was no deviation of more than 0.02 pH units. Also, paired samples checked within a few hundredths of a pH unit, so that we estimate our pH measurement error at not more than ± 0.03 pH units. The feldspar–water and mica–water suspensions were stirred vigorously with magnetic stirrers; temperatures were measured at frequent intervals but not controlled. In the determination of temperature coefficients, the reaction vessels were immersed in hot water and then cold water, and temperatures were correlated with pH readings by frequent measurements during the heating and cooling cycle.

In a typical experiment, a weighed amount of ground feldspar or mica was added to 200 ml of rapidly stirred water that had been deaerated as quickly as possible to minimize KCl contamination from the salt bridge of the saturated calomel electrode. Nitrogen was bubbled slowly through the solutions throughout the experiment; the rate was increased just prior to each addition of reagents to prevent air contamination during addition. After addition of feldspar or mica, KCl solution saturated at 25°C was added by pipette at various intervals depending on the time necessary to achieve constant pH.

Results

A. ADULARIA

The pH *of suspensions as a function of amount of material used.*—Various weights of ground adularia were added to water, and the equilibrium pH was determined. Figure 4 shows the results. A hundredfold increase in surface area causes an increase of about one pH unit (tenfold decrease in a_{H^+}). Measurement of the more concentrated suspensions was made in a small water volume. Results from use of wt. feldspar/wt. water greater than 1/1 were not included because of the uncertainty of pH measurements in such thick suspensions. The pH increased with every addition in the range studied.

Titration curves with KCl.—Most of the work was confined to the reaction of a 1 percent suspension (2 g adularia/200 ml H_2O) with added K^+, although 0.25 percent and 6 percent suspensions were also tested. After the adularia was added to water, KCl solution saturated at 25°C was added in small increments. After each addition, the pH was allowed to come to " equilibrium," the measure of equilibrium being a constant pH value for a period of five minutes or more. In general, the reaction was rapid; there was little variation in pH thirty seconds after addition of KCl. At various stages of total KCl concentration, the containers were heated and were allowed to come to constant pH at a higher temperature; this temperature ranged up to 65°C. A series of such heating experiments showed that the temperature

coefficient of pH is nearly linear between 25° and 65°C, and is -0.016 ± 0.002 pH units per °C.

The experimental results are given in Table 2. The molality of KCl was used to calculate activity of K^+ on the assumption that the mean activity coefficient of KCl ($\gamma \pm$ KCl) is the same as that for K^+ and for Cl^-. Values for $\gamma \pm$ KCl were obtained from Harned and Owen (1950, p. 369). The
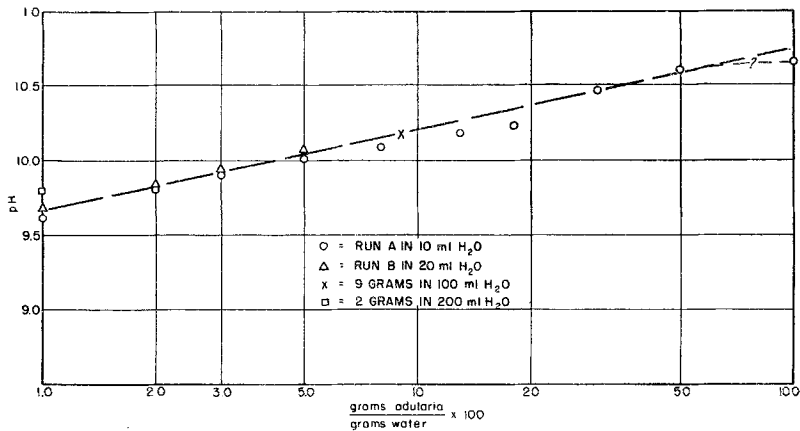

FIGURE 4.—Graph showing pH of various wt.-percent suspensions of ground adularia in water.

tabulated results are shown graphically in Fig. 5. We debated using m_{KCl} instead of calculated $^aK^+$ values for our plots and calculations, but decided that inasmuch as pH measures a_{H+}, we should attempt to keep K^+ in the same units. Neither method is entirely satisfactory, as will be shown later. The values for m_{KCl} were calculated from the amount of KCl *added*; the concentrations used were always so large that K^+ from the feldspar or from the calomel electrodes was negligible.

B. MICA

The pH *of suspensions as a function of amount of material used.*—Figure 6 shows the relation between pH and weight of mica added to pure water. In contrast to feldspar, mica suspensions attain constant pH at relatively low weight percent values. The slope of the curve, in the region preceding constancy, is steeper than that for feldspar and suggests a direct proportionality between log weight of mica added (surface added) and increase in pH.

"Titration curves" with KCl.—Suspensions containing 1 wt.-percent mica or more gave similar curves when titrated with KCl. A curve at lower pH was obtained from a 0.11 wt.-percent suspension.

Numerous runs were made to determine the temperature coefficient of the reactions. The value of -0.016 ± 0.002 pH units per °C was obtained—a

Table 2.—" Titration " of Adularia Suspensions with KCl

pH	Temp. (°C)	pH 25°C*	m_{KCl}	γ_{KCl}	$\log a_{K^+}$	Remarks
A	0.25 Wt.-percent Suspension of − 200-mesh Adularia (0.5 g/200 ml)					
9.11	28.0	9.16	—	—	—	Highest pH reached.
8.92	28.0	8.97	0.0053	0.929	−2.31	
8.65	32.8	8.77	0.0105	0.900	−2.02	
8.51	33.1	8.64	0.021	0.868	−1.74	
8.36	33.7	8.50	0.042	0.829	−1.46	
8.19	34.1	8.33	0.083	0.782	−1.19	
8.10	35.0	8.24	0.125	0.750	−1.03	
B_1	1.00 Wt.-percent Suspension of − 200-mesh Material (2.0 g/200 ml)					
9.78	30.0	9.86	—	—	—	Highest pH reached.
9.21	30.0	9.29	0.0420	0.829	−1.46	
9.06	31.0	9.16	0.083	0.782	−1.19	
8.94	32.7	9.06	0.125	0.750	−1.03	
8.85	33.5	8.99	0.163	0.730	−0.92	
8.79	33.8	8.93	0.203	0.715	−0.84	
8.69	34.0	8.83	0.297	0.687	−0.69	
8.60	34.0	8.74	0.389	0.663	−0.59	
8.49	34.0	8.63	0.561	0.633	−0.45	
8.38	34.4	8.53	0.721	0.612	−0.36	
B_2	1.00 Wt.-percent Suspension of − 200-mesh Material (2.0 g/200 ml)					
9.31	26.0	9.33	0.042	0.829	−1.46	
9.18	26.0	9.20	0.083	0.782	−1.19	
9.08	26.0	9.10	0.125	0.750	−1.03	
9.00	26.0	9.02	0.163	0.730	−0.92	
8.95	26.0	8.97	0.198	0.718	−0.85	
8.90	26.0	8.92	0.241	0.699	−0.77	
8.78	28.0	8.83	0.315	0.681	−0.67	
8.69	28.0	8.74	0.385	0.665	−0.59	
B_3	1 Wt.-percent Suspension of − 200-mesh Adularia (2.09 g/200 ml)					
9.50	28.0	9.55	0.021	0.868	−1.74	
9.32	28.0	9.37	0.042	0.829	−1.46	
9.18	28.0	9.23	0.083	0.782	−1.19	
C	6.0 Wt.-percent Suspension of − 200-mesh Adularia (9 g/150 ml)					
10.21	29.0	10.27	—	—	—	Highest pH reached.
9.96	29.0	10.02	0.017	0.878	−1.82	
9.85	29.0	9.91	0.035	0.840	−1.55	
9.72	30.0	9.80	0.067	0.787	−1.28	
9.55	30.0	9.63	0.132	0.745	−1.00	
9.48	30.0	9.56	0.197	0.718	−0.85	
9.40	30.0	9.48	0.258	0.698	−0.74	
9.34	30.0	9.42	0.319	0.678	−0.68	
9.18	30.0	9.26	0.598	0.628	−0.43	
9.01	32.0	9.12	0.845	0.600	−0.30	
8.94	30.4	9.03	1.07	0.582	−0.21	
8.80	32.6	8.92	1.44	0.566	−0.088	

The tabulated results are plotted in Figure 5.

* Temperature coefficient used to correct pH values to 25°C = −0·016 pH/°C on all runs.
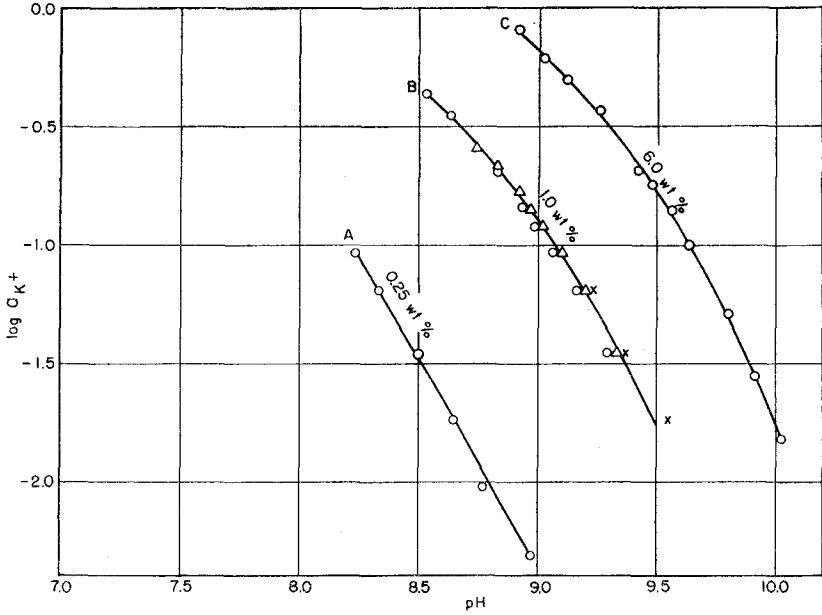
FIGURE 5.—Observed titration curves for various wt.-percent suspensions of
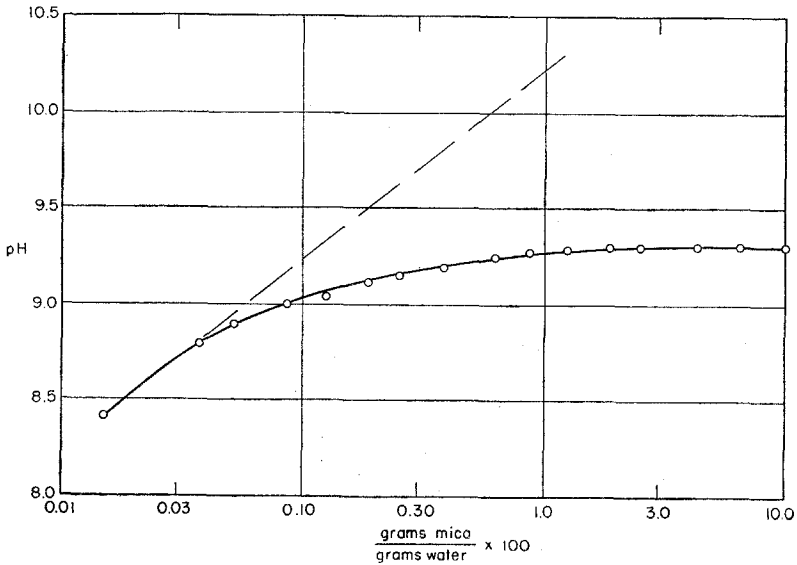adularia ; pH values corrected to 25°C.

FIGURE 6.—Graph showing pH of various wt.-percent suspensions of
ground mica in water.

result identical with that for adularia. The experimental results are given in Table 3 and are shown graphically in Fig. 7.

Discussion

A. ADULARIA

The curves of Fig. 5 show that the reaction of adularia with water is surface-dependent, for the greater the amount of ground adularia in a given amount of water, the higher the pH achieved at a given excess potassium ion
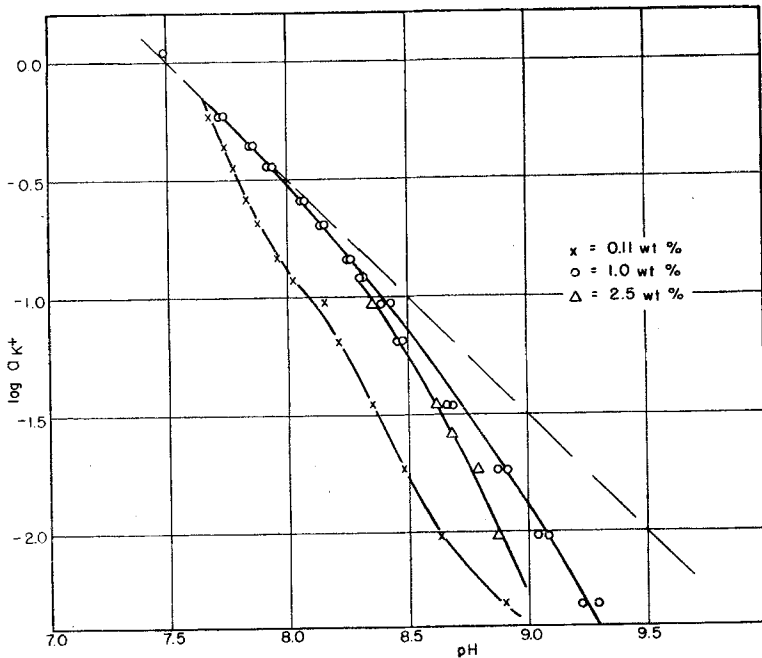

FIGURE 7.—Observed titration curves for various wt.-percent suspensions of mica ; pH values corrected to 25°C.

concentration. This relation corroborates Tamm's (1930) work on microcline suspensions (Fig. 3), which shows increasing amounts of $K^+ + Na^+$ released to solution with increasing pH, and our own results on the equilibrium pH of various weight-percent suspensions of adularia in pure water (Fig. 4). Because K^+ is released to solution, the exchange can not simply be adsorption of H^+ on the feldspar surface ; H^+ must proxy for K^+ and release it to solution.

TABLE 3.—" TITRATION " OF MICA SUSPENSIONS WITH KCl

pH	Temp. (°C)	pH 25°C*	m_{KCl}	γ_{KCl}	$\log a_{K^+}$	Remarks
A	0.11 Wt.-percent Suspension of — 200-mesh Material (0.23 g/200 ml)					
9.30	26.8	9.33	—	—	—	Highest pH reached.
8.95	26.8	8.98	0.0053	0.929	−2.31	
8.50	33.0	8.63	0.0105	0.900	−2.02	
8.34	33.8	8.48	0.021	0.868	−1.74	
8.21	34.0	8.35	0.042	0.829	−1.46	
8.05	34.8	8.21	0.083	0.782	−1.19	Pronounced drift on many
7.99	35.0	8.15	0.125	0.750	−1.03	readings, probably be-
7.88	34.0	8.02	0.163	0.730	−0.92	cause of small amount
7.81	33.8	7.95	0.202	0.715	−0.84	mica used.
7.73	33.5	7.87	0.297	0.687	−0.69	
7.69	33.8	7.83	0.389	0.663	−0.59	
7.63	34.5	7.78	0.561	0.632	−0.45	Drift erratic—mean pH
7.59	34.1	7.74	0.721	0.612	−0.36	values used.
7.53	33.8	7.67	1.01	0.586	−0.23	
B_1	1.0 Wt.-percent Suspension of — 200-mesh Material (2 g/200 ml)					
9.80	24.5	9.79	—	—	—	Highest pH reached.
9.23	24.5	9.22	0.0053	0.929	−2.31	
9.03	25.3	9.04	0.0105	0.900	−2.02	Highest pH read is mo-
8.86	25.8	8.87	0.021	0.868	−1.74	mentary value ; has
8.64	26.2	8.66	0.041	0.829	−1.46	rapid downward drift.
8.42	26.7	8.45	0.083	0.782	−1.19	pH values after addi-
8.29	31.0	8.39	0.125	0.750	−1.03	tion excess KCl steady
8.20	31.0	8.30	0.163	0.730	−0.92	for times up to 2 hours.
8.14	31.5	8.24	0.202	0.715	−0.84	
8.02	32.0	8.13	0.297	0.687	−0.69	
7.94	32.0	8.05	0.389	0.663	−0.59	
7.80	32.0	7.91	0.561	0.632	−0.45	
7.72	31.5	7.83	0.721	0.612	−0.36	
7.62	30.9	7.71	1.01	0.586	−0.23	
7.41	29.0	7.47	2.00	0.55	+0.04	
B_2	1.0 Wt.-percent Suspension of — 200-mesh Material (2 g/200 ml)					
9.78	23.5	9.76	—	—	—	Highest pH reached.
9.31	24.0	9.29	0.0053	0.929	−2.31	
9.10	24.2	9.08	0.0105	0.900	−2.02	
8.92	24.5	8.91	0.021	0.868	−1.74	
8.70	24.8	8.69	0.041	0.829	−1.46	
8.48	27.0	8.48	0.083	0.782	−1.19	
8.38	28.0	8.43	0.125	0.750	−1.03	
8.26	29.0	8.31	0.163	0.730	−0·92	
8.20	29.0	8.26	0.202	0.715	−0.84	
8.08	29.5	8.15	0.297	0.687	−0.69	
7.99	29.5	8.06	0.398	0.663	−0.59	
7.86	29.5	7.93	0.561	0.632	−0.45	
7.78	29.5	7.85	0.721	0.612	−0.36	
7.67	29.5	7.74	1.01	0.586	−0.23	
7.46	29.0	7.48	2.00	0.55	+0.04	

TABLE 3—*cont.*

C   2.5 Wt.-percent Suspension of −200-mesh Material (2.5 g/100 ml)

8.77	31.8	8.88	0.0105	0.900	−2.02
8.67	31.8	8.78	0.021	0.868	−1.74
8.57	31.8	8.68	0.031	0.850	−1.59
8.50	31.8	8.61	0.041	0.829	−1.46
8.35	31.7	8.46	0.083	0.782	−1.19
8.24	31.7	8.35	0.125	0.750	−1.03
8.24	31.7	8.35	0.125	0.750	−1.03 . . . . Added mica to make 3.7% suspension.

D   Various Wt.-percent Suspensions.

Mica was supended in KCl solutions of various concentrations.

When mica was originally in excess of 1 wt. percent, addition of more mica—up.to several wt. percent—did not change the pH.
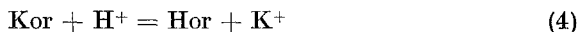
* Temp. coefficient used to correct pH values to 25°C = − 0.016 pH/°C on all runs.

The simplest mechanism of reaction would be of the type :

$$\text{Kor} + \text{H}_2\text{O} = \text{Hor} + \text{OH}^- + \text{K}^+$$

(where Kor = potassium orthoclase ; Hor = hydrogen orthoclase)
  or

$$\text{Kor} + \text{H}^+ = \text{Hor} + \text{K}^+ \tag{4}$$

in which one K^+ and one OH^- would be released for each H^+ used up. Tamm's data (Fig. 3) show that this cannot be the only reaction at high pH, for K^+ ($\text{K}^+ + \text{Na}^+$) is not equivalent to OH^- ; instead the ratio of K^+ to OH^- increases rapidly at high pH values.

From another point of view, Tamm's data show that the cations released at high pH are considerably in excess of OH^-, so that, to maintain electrical neutrality in the suspension, the cations in excess of OH^- must be balanced by some other negatively charged ion or surface. For example, at pH 10.68, OH^- is $10^{-3.32}$, whereas total cations are $10^{-2.23}$, showing that less than one-tenth of the released K^+ and Na^+ are balanced by OH^-. The best interpretation of Tamm's data (heavy dashed line on Fig. 3) suggests that below pH 10, $\text{OH}^- \simeq (\text{K}^+ + \text{Na}^+)$, indicating that the dominant reaction may be of the simple type suggested (equation 4), whereas above pH 10 another reaction comes into ascendancy. The dotted line on Fig. 3 shows the relation expected between $(\text{K}^+ + \text{Na}^+)$ and OH^- if the only reaction occurring is that of equation (4). The lower OH^- values actually observed (heavy dashed line) suggest some type of " back reaction " that uses up OH^-, or the presence of a negatively charged surface or negatively charged ion in solution.

Thus, the reactions involved can be considered to be simple cation substitution releasing K^+ and forming a hydrogen orthoclase (Hor), followed by a dissociation at pH > 10 to give a negative ion or surface.

Because most of our work was done below pH 10, we decided, as a first approximation, to analyze the reaction as if it were :

$$\text{Kor} + \text{H}^+ = \text{Hor} + \text{K}^+.$$
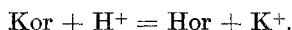
H^+ and K^+ are species dissolved in the suspending water, but a question
  6

arises concerning the nature of Kor and Hor. Should they be treated as solids or as exchange substrates (essentially as solvents)? Clearly both Hor and Kor cannot be bulk solids, for their concentration (activity) would remain constant during the reaction and the equilibrium constant would be of the form :

$$k = \frac{a_{K^+}}{a_{H^+}} \tag{5}$$

Such a constant would be a straight line on a plot of log a_{K^+} against pH, as shown by line no. 1 in Fig. 8. Furthermore, if equilibrium were attained with solid Kor and Hor, the position of the line would be fixed at constant temperature and pressure and would not shift with changing amounts of suspended solid.

Therefore, the activity of Kor or Hor or both is changing. Our first guess was that the ground feldspar was behaving like a clay suspension; that is to say that placing the feldspar in water permitted H^+ to substitute for K^+ on the surface, and that back-titration with K^+ replaced the H^+ ions in such a way as to maintain a ratio of H^+-saturated surface to K^+-saturated surface essentially proportional to the ratio of a_{H^+} in solution to a_{K^+} in solution. This is tantamount to saying that both Kor and Hor concentrations vary with changing H^+ and K^+ in solution. The expression for an exchange of this type would be written :

$$\frac{a_{K^+}[\text{Hor}]}{a_{H^+}[\text{Kor}]} = k \tag{6}$$

In Fig. 8 line no. 3 shows the curve to be expected from such behavior. The line is drawn on the assumption that the concentration of Hor is equal to the $[OH^-]$ in the solution, and that the concentration of Kor is equal to the $[OH^-]$ of original hydrolysis minus the $[OH^-]$ at any given point on the excess K^+ titration curve. Thus it is assumed that each K^+ displaced from the surface by reaction with water yields one OH^-, and that as K^+ is restored OH^- disappears from solution. We have designated the $[OH^-]$ resulting from original hydrolysis as Kor°, for we regard it as a measure of the original reactive surface of the feldspar under conditions where one K^+ and one OH^- are released for each H^+ bound. Our data do not fall on such a curve, but lie between it and the straight line expected if both Kor and Hor are solids of fixed composition.

The observed titration curve, at high added KCl, has very nearly a $-45°$ slope; thus there is little change in the ratio of [Kor] to [Hor] in that part.

A lack of change of [Kor] is understandable, inasmuch as the K^+ surface would be expected to be almost completely restored by addition of KCl, but H^+ appears in solution with increasing KCl, so that [Hor] must decrease if it is behaving as an exchange substrate. The simplest explanation seems to be to assume that [Hor] is constant throughout the titration. If so, the exchange constant reduces to :

$$\frac{a_{K^+}}{a_{H^+}[\text{Kor}]} = k \tag{7}$$
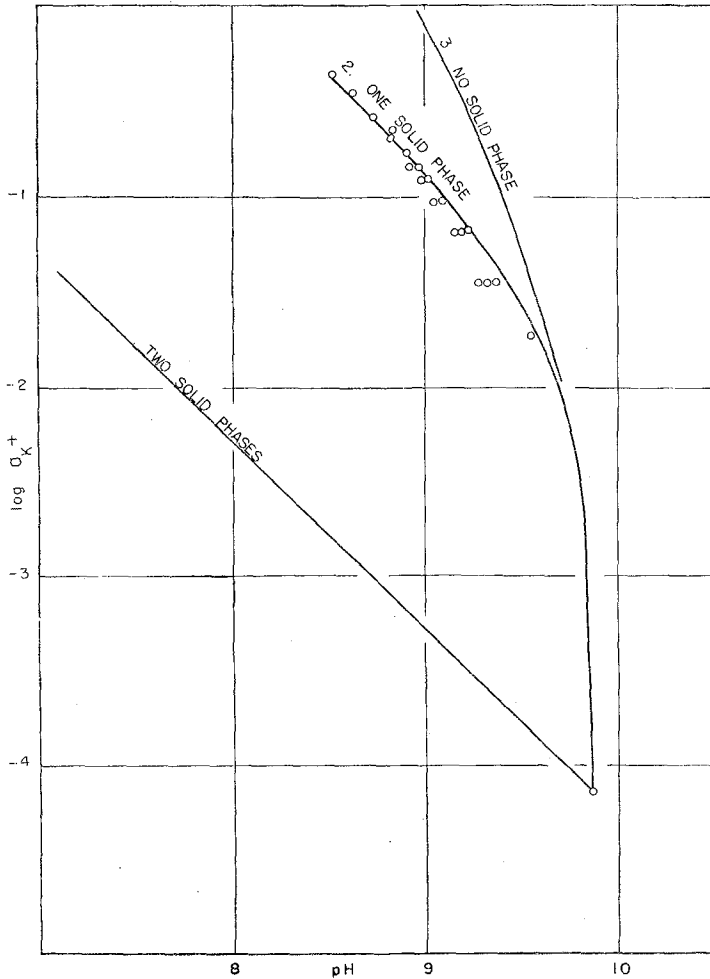
FIGURE 8.—Comparison of theoretical and experimental values for the equation: Kor + H+, assuming (1) Both Kor and Hor are solids of constant activity,

$$k = \frac{[\text{K}^+]}{[\text{H}^+]};$$

(2) that Hor only is a solid of constant activity,

$$k = \frac{[\text{K}^+]}{[\text{H}^+][\text{Kor}]};$$

and (3) that neither Kor nor Hor is a solid of constant activity,

$$k = \frac{[\text{K}^+][\text{Hor}]}{[\text{H}^+][\text{Kor}]}.$$

Curve no. 2 on Fig. 8 has been calculated on this assumption. In making calculations it is assumed as before that [Kor°] is equal to the a_{OH^-} resulting from original hydrolysis, and that [Kor] is equal to [Kor°] $- a_{OH^-}$ at any given point on the KCl titration curve.

The experimental data are fitted by the calculated curves within the limit of error.

In Fig. 9, the relation between the experimental results for the three suspensions studied, and curves calculated on the basis of the reaction constant from equation (7) are shown. The fit is reasonably good. Deviation from the calculated curves is chiefly at high pH, where the calculated curve for the 6 wt.-percent suspension lies to the right of the observed points at low KCl concentrations. This indicates that substitution of a_{OH^-} resulting from hydrolysis for [Kor°] is too small. This relation is consistent with Tamm's observation (Fig. 3) that released bases exceed a_{OH^-} at pH values above 10.

The closeness of the fit is also somewhat unexpected because the *concentration* of Kor was used. In exchange constants, which contain a ratio of concentrations $\left(\text{i.e. } \dfrac{[Kor]}{[Hor]} \right)$, it is commonly assumed that the ratio of the concentrations is nearly equal to the ratio of the activities, because the activity coefficients are for similar species and have comparable (if unknown) values. Thus:

$$\frac{a_{Kor}}{a_{Hor}} = \frac{\gamma_{Kor}[Kor]}{\gamma_{Hor}[Hor]}$$

but:

$$\gamma_{Hor} \cong \gamma_{Hor}$$

so:

$$\frac{a_{Kor}}{a_{Hor}} \sim \frac{[Kor]}{[Hor]}$$

Presumably the reasonable fit indicates that the activity coefficient of Kor does not change markedly with change of ionic strength of the solution.

In summary, the hydrolysis-titration data are fitted fairly well if it is assumed that the major reaction is substitution of H^+ for K^+ at the feldspar surface, releasing one OH^- from water for every K^+ released (at pH values < 10). The H-feldspar behaves like a crystalline solid to the extent that it appears to maintain constant concentration, whereas the K-feldspar behaves like a typical exchange substrate with a concentration ranging from nearly zero to a value approximately proportional to the amount of surface introduced. In a formal sense the reaction can be written as if Kor were a dissolved molecular species, Hor a solid of fixed composition, and H^+ and K^+ dissolved ions.

This essentially empirical curve-fitting is in accord with the physical picture of the reaction process drawn by Nash and Marshall (1956a, 1956b). They deduce a surface zone of disruption as a result of hydrogen ion attack on feldspar, with a gradation downward into a little-changed feldspar frame-

work into which hydrogen ions have diffused. Correns and Von Engelhardt (1938) have a similar concept and show that the rate of thickening of the acid reaction film corresponds to that of a solid state diffusion process. In our short-term experiments we visualize that a feldspar grain in water develops a broken-up surface layer that grades downward into a zone where H^+ ions occupy K^+ positions, protecting the interior of the grain from further attack, and presenting a thin layer of " crystalline " Hor to the external solution.
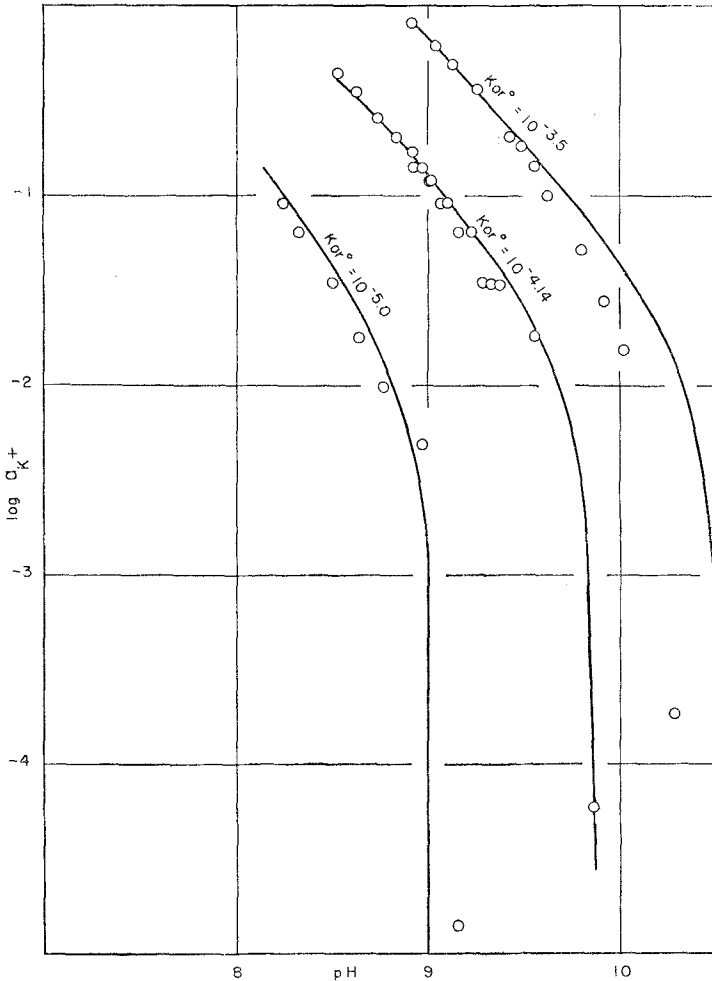

FIGURE 9.—Comparison of titrations of 0.25 wt.-percent, 1.0 wt.-percent, and 6 wt.-percent feldspar suspensions. Circles are experimental, lines are calculated from the equation,

$$\frac{a_{K^+}}{a_{H^+}[Kor]} = 10^{12.3}.$$

Eventually the disrupted zone loses silica and alumina to the solution but still leaves an aluminous silicious residue (Correns and Von Engelhardt, 1938), so that the time necessary for equilibrium to be attained between bulk crystalline K or and solution may be long even in terms of geologic periods.

B. MICA

In distinction to adularia, the reaction of mica with water reaches an equilibrium pH at low wt.-percent suspensions (Fig. 6). Furthermore, insofar as we can determine, the slope of the pH–log wt.-percent line is 45 degrees in the region preceding equilibrium, indicating that the major reaction involved is straightforward H^+–K^+ substitution. All the titrations carried out with 1 wt.-percent or higher suspensions gave essentially the same curve, and additions of mica to suspensions containing various concentrations of added KCl caused no pH change. Presumably, then, the reaction taking place is :

$$\text{K-mica} + H^+ = \text{H-mica} + K^+$$

At suspensions of 1 wt. percent and above, the reaction, as measured by the pH, is independent of the amount of mica present. If so, the titration curves, as shown on Fig. 7, should be straight lines with slopes of -45 degrees. This is true at high values of added KCl, but there is significant deviation from linearity at low added KCl. Furthermore, a considerable spread of pH values was obtained at low added KCl for various suspensions, so that there may be hydrogen ions held in a variety of sites on the mica plate surfaces and edges. For example, if the hydrolysis pH is obtained by successive small additions of mica to water, the curve shown in Fig. 6 is obtained. On the other hand, if a large amount of mica is added to pure water, the original pH may rise to 10 or even slightly higher. Then a pronounced downward drift takes place, with pH eventually settling in the vicinity of 9.3 (the maximum achieved by the other method). This lowering of pH can be achieved quickly by addition of a very small concentration of KCl(0.0005M). At the moment, we attribute this original high pH to weak H^+ adsorption on the edges of the minute mica flakes; with release of K^+ from the mica itself, or by addition of a small amount of KCl, these hydrogens are discharged, and the resulting pH (9.3) represents H^+–K^+ exchange chiefly on the plate surfaces.

Because the mica reaction is independent of the amount of mica present, we assumed that the equilibrium constant for the reaction is :

$$\frac{(\text{H-mica}) (K^+)}{(\text{K-mica}) (H^+)} = \frac{(K^+)}{(H^+)} = k_{\text{mica}}$$

From the high KCl portion of the titration curves of Fig. 7 a value for k of $10^{+7.4 \pm 0.2}$ is obtained.

We can not explain the deviation of the low KCl part of the curve from a straight line.

C. RELATION OF HYDROLYSIS TO TRUE EQUILIBRIUM

The hydrolysis reactions studied can be thought of as a first step in the change of K-feldspar to K-mica, and of K-mica to kaolinite. Their chief value is to show the remarkable avidity of hydrogen ion for the Al–Si–O framework of K-feldspar and K-mica. The low concentration of H^+ in pure water at room temperature is sufficient for rapid release of K^+ from these minerals. In mica, this attack apparently ceases when the K^+/H^+ activity ratio in the suspending medium reaches a value of about $10^{7.4}$ It has not been possible to determine the limiting ratio for feldspar, presumably because fixation of advancing H^+ prevents a further attack and the grains become armored. However, Tamm (1930) produced suspensions with a $\dfrac{K^+}{H^+}$ ratio of $10^{8.4}$, and in our most concentrated suspension (6 wt.-percent) the ratio, although variable with added KCl, ranged up to about $10^{8.8}$. From another aspect, the feldspar always behaved as if a surface (or near surface) film of solid H-orthoclase were present, so that the reconversion of the H-orthoclase back to K-orthoclase was not accomplished at any ratios of K^+ to H^+ used; thus K^+ is highly ineffectual in competing with H^+.

These results are consistent with the absence of orthoclase as a primary sedimentary chemical precipitate. It could form only if K^+ could compete successfully with H^+ for positions in the feldspar structure, and this condition could be realized only in environments low in H^+ (pH 10.5?) and high in K^+ (10^{-1}?). Sedimentary mica, on the other hand, would not require quite such extreme conditions.

Also, the hydrolysis experiments indicate that the big energy change in the reaction from feldspar to mica plus silica, and from mica to kaolinite, must be in the displacement of the cations, for the equilibrium constants for these reactions also depend on the ratio of the activities of K^+ to H^+. The hydrolysis is so vigorous that there is little energy left over, so to speak, for structural rearrangement, hydration or ejection of silica, if the true equilibrium reactions are to occur anywhere near the conditions we can deduce from weathering relations, or from extrapolation from higher temperature occurrences.

As a reasonable estimate the equilibrium constant for the reaction (25°C, 1 atmosphere):

$$3\,\text{K-feldspar} + 2\,H^+ = \text{K-mica} + 6\,SiO_2 + 2\,K^+$$
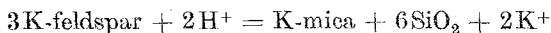
$$k = \frac{a_{K^+}^2}{a_{H^+}^2}$$

is approximately 10^{19} (pH 10.5, $a_{K^+} = 10^{-1}$), whereas that for the reaction:

$$2\,\text{K-mica} + 2\,H^+ + 3\,H_2O = 3\,\text{kaolin} + 2\,K^+$$
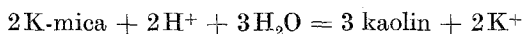
$$k = \frac{a_{K^+}^2}{a_{H^+}^2}$$

is approximately 10^{15} (pH $= 9.5$, $a_{K^+} = 10^{-2}$).

These equilibrium constants would give standard free energies for the reactions of approximately -26 kcal and -20 kcal respectively. It is notable that these rough values are not particularly sensitive to the specific conditions chosen.

The temperature coefficients of these reactions must be very steep, for adularia forms in mildly alkaline hot springs (pH $= 8.5$, $a_{K^+} = 10^{-3}$), and mica is stable in strong acid (pH $= 1$) at 350°C (Gruner, 1944). This suggests that the other cations become better competitors with H^+ at elevated temperatures and pressures so that at a given pH the kaolinites give way to the micas, and the mica in turn to three-dimensional silicates, as temperature and pressure increase.

The same trend was found in the hydrolysis reactions, which moved to lower pH at constant a_{K^+} with increasing temperature. However, the slope (-0.016 pH units per °C) is probably flatter than that for equilibrium between the bulk minerals.

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