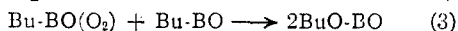


oxidize monomeric butylboron oxide to form the metaborate in a reaction analogous to the interaction of benzoyl hydrogen peroxide with benzaldehyde to give two molecules of benzoic acid (3).



Some evidence in support of the intermediate peroxide is gained from experiments with partially oxidized butylboron oxide which show that it liberates iodine from alcoholic potassium iodide and catalyzes the polymerization of vinyl acetate as do other peroxides.

Efforts to establish a reaction mechanism on the basis of kinetic measurements were unsuccessful. When a sample of *n*-butylboron oxide was exposed to oxygen without agitation, the rate of oxygen absorption followed the unimolecular law as shown by the straight line in Fig. 2 obtained by plotting the logarithm of the concentration of *n*-butylboron oxide against time. The concentration of *n*-butylboron oxide was determined on the basis of the oxygen consumed in accordance with equation (1). This agreement with the unimolecular law is superficial, however, because mechanical agitation of the reaction mixture in other experiments not only increased the rate of oxidation but gave data which could not be interpreted kinetically. Apparently the rate of diffusion of unoxidized material to the surface of the reaction mixture is the rate-determining step in the absence of agitation.

The effect of catalysts on the rate of oxidation was observed in experiments with cobalt linoleate and ammonium vanadate as positive catalysts, and hydroquinone and phenyl- $\beta$ -naphthylamine as typical anti-oxidants. The only one of these catalysts which had an appreciable effect on the rate of oxidation was phenyl- $\beta$ -naphthylamine, which inhibited the reaction almost completely. It is interesting to note that aromatic amines are more effective anti-oxidants than phenols for aliphatic aldehydes.<sup>14</sup> This is a further point of resemblance between the alkylboron oxides (or boronic acids) and aliphatic aldehydes, Johnson, *et al.*,<sup>2</sup> having already pointed out that both types of compounds combine with oxygen, reduce ammoniacal silver oxide, and form cyclic trimers.

### Summary

*n*-Butylboron oxide undergoes quantitative oxidation and depolymerization in the presence of dry oxygen to form monomeric *n*-butyl metaborate. There is evidence for the intermediate formation of a peroxidic substance. A possible reaction mechanism has been suggested, but could not be confirmed by rate measurements because the kinetics were complex. Phenyl- $\beta$ -naphthylamine retards the oxidation but hydroquinone does not.

(14) Bailey, *Proc. Royal Irish Acad.*, **45B**, 373 (1939).

CLEVELAND, OHIO

RECEIVED MARCH 23, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF SOILS, UNIVERSITY OF MISSOURI]

## The Electrochemical Properties of Mineral Membranes. V. Beidellite Membranes and the Determination of Sodium<sup>1</sup>

BY C. E. MARSHALL<sup>2</sup> AND C. A. KRINBILL<sup>2</sup>

### Introduction

Previous papers in this series<sup>3</sup> have dealt with the use of preheated montmorillonite membranes in the potentiometric determination of potassium and ammonium and with the application of this method to the electrochemical study of colloidal systems as typified by the clays. The hydrogen

montmorillonite membranes used were preheated to 490°. This treatment conferred remarkable properties of stability and selectivity. The membranes were of high resistance (1-10 megohms), yet showed excellent reproducibility toward potassium and ammonium ions. Acids attacked them chemically and highly reproducible values could only be obtained at pH values above 4. Sodium salts alone gave poor reproducibility and asymmetry potentials were troublesome. However, mixtures of sodium and potassium salts measured against potassium chloride as standard gave values which suggested that the

(1) Contribution from the Department of Soils, Missouri Agricultural Experiment Station, Journal Series No. 820. Read before the Colloid Chemistry Division at the 103rd meeting of the American Chemical Society in Memphis on April 23, 1942.

(2) Associate Professor and Research Assistant in Soils, respectively.

(3) Marshall and Bergman, *THIS JOURNAL*, **63**, 1911 (1941); *J. Phys. Chem.*, **46**, 52 (1942); **46**, 325 (1942).

membrane was definitely sensitive to sodium ions and that both the mobility and the activity of the sodium were concerned in the establishment of the potential difference. These membranes possessed also the remarkable property of being insensitive to divalent and trivalent cations.

In an attempt to improve the conditions for the potentiometric estimation of sodium, W. E. Bergman in this Laboratory prepared hydrogen montmorillonite membranes (Wyoming bentonite, electrolyzed fraction  $< 0.2 \mu$ ) preheated to  $350^\circ$ . These were found to lose their asymmetry potentials readily on soaking in  $N$  sodium chloride solution and then in  $0.1 N$  solution. They gave potentials, for concentrations below  $0.1 N$ , which agreed well with those calculated from the Nernst equation.

It was later found that these  $350^\circ$  membranes have quite different properties of ionic selectivity than those heated to  $490^\circ$ . They have a much lower resistance when wet, 5–20,000 ohms as against 1–10 megohms for the latter. They are sensitive to divalent cations as well as to monovalent. Hence their ionic behavior is qualitatively similar to that of chabazite and apophyllite membranes.<sup>4</sup> They have the advantages over the latter of easier preparation, of greater reproducibility and of lower resistance. However, a distinctly selective character is still present. Unlike the beidellite membranes described below, they are not sensitive to trivalent cations such as cerium.

In an attempt to secure even greater reproducibility toward sodium, membranes were prepared from another clay mineral, colloidal beidellite.<sup>5</sup> These membranes, whose preparation and properties are herein described, act as general cationic membranes. By their use we can look forward to the estimation of monovalent, divalent and possibly trivalent cations in pure solution. The present contribution is concerned chiefly with sodium. The application to calcium and other polyvalent cations will be considered in a later communication.

### Experimental

**Preparation of Membranes.**—The beidellite membranes were prepared using essentially the same procedure as has been described for those of montmorillonite. The starting point was the heavy subsoil or B horizon of the Put-

(4) Marshall, *J. Phys. Chem.*, **43**, 1155 (1939).

(5) The preparation and properties of clay films were first described by Hauser and le Beau [*ibid.*, **42**, 961 (1938)], who used bentonite clay.

nam silt loam soil taken from an experimental field at Moberly, Missouri. This is a calcium–hydrogen soil containing little organic matter. After treatment with hydrogen peroxide to remove the organic matter, the soil suspension in water was dispersed by adding sodium hydroxide to a  $pH$  of 7. The clay fraction was decanted after standing for twenty-four hours or more, and was then passed through a Sharples supercentrifuge running at 30,000 r. p. m., at such a rate of flow that all particles larger than  $0.2 \mu$  in equivalent spherical diameter were retained. The suspension of  $< 0.2 \mu$  clay which passed on was then concentrated by electrolysis, the process being continued until all sodium and calcium were removed. The electrolyzed clay was then diluted to 1–2% concentration. It was dispersed by being mechanically stirred for fifteen minutes at high speed and was then boiled to remove dissolved air. The hot suspension was poured into a shallow copper tray which had previously been rubbed over with a cloth saturated with neutral mineral oil. Evaporation was effected at about  $80^\circ$  by heating from above with an electric radiator. In this way a layer of suspension 1–2 cm. in depth evaporates to dryness and leaves a clay film 0.2–0.3 mm. in thickness which readily can be removed. This film consists of the mineral beidellite,<sup>6</sup> a clay of the montmorillonite group, but having a somewhat lower base exchange capacity than montmorillonite itself.

The beidellite film is less flexible than that of montmorillonite and, instead of using a cork borer, the membrane disks are prepared by breaking off corners from irregular fragments. They show some tendency to split or cleave parallel to the surface. They were mounted on the ground ends of 8-mm. Pyrex tubing with hard de Khotinsky cement or plicene. Once mounted they showed remarkable stability and on soaking for only a few hours in salt solutions the asymmetry potentials disappeared. Over 90% of the membranes thus prepared gave reproducible potentials close to the anticipated values. Deviations of 1 millivolt were rarely found. Differences between individual membranes were most marked in the more concentrated and in the very dilute solutions.

The potentials were determined using saturated calomel electrodes with agar bridges on each side of the membrane. A known solution was placed inside the tube as standard. In some cases a silver chloride electrode was used with a standard chloride solution inside the membrane tube and a saturated calomel cell in the outer solution.

Special care was taken to make the liquid junction potentials as small and reproducible as possible. It was found, for instance, that a liquid junction potential of several millivolts could arise when a saturated calomel electrode with upturned agar tip was transferred from one solution of a sodium salt to another of different concentration. The reason for this was that in the first solution some potassium chloride was lost by diffusion and replaced by a more dilute mixture of potassium and sodium salts. This gave a junction potential against a second sodium salt solution; it diminished with time as more potassium chloride diffused toward the tip.

In making the final measurements, therefore, a calomel

(6) Marshall, *Zeitschr. Kryst.*, **A90**, 8 (1935); **A91**, 433 (1935); Marshall, *J. Phys. Chem.*, **41**, 935 (1937).

cell was always used whose tip had been for some time in contact with saturated potassium chloride solution. A Leeds and Northrup thermionic amplifier was used in conjunction with a calibrated "student" type potentiometer and individual measurements were made to 0.1 millivolt. The amplifier could be dispensed with where the total resistance was less than 20,000 ohms. The resistances were determined approximately by applying a known voltage and measuring the current.

**Comparison of Membranes.**—The qualitative characteristics of membranes prepared in different ways are given in Table I.

It is evident that the effect of heat on the membrane characteristics is quite different for the two minerals. Further work will be needed to establish the exact causes of these differences in sensitivity to different cations.

In making quantitative comparisons of different membranes it is necessary to use a single salt such as potassium chloride. For details of the graphical method employed see ref. 3.

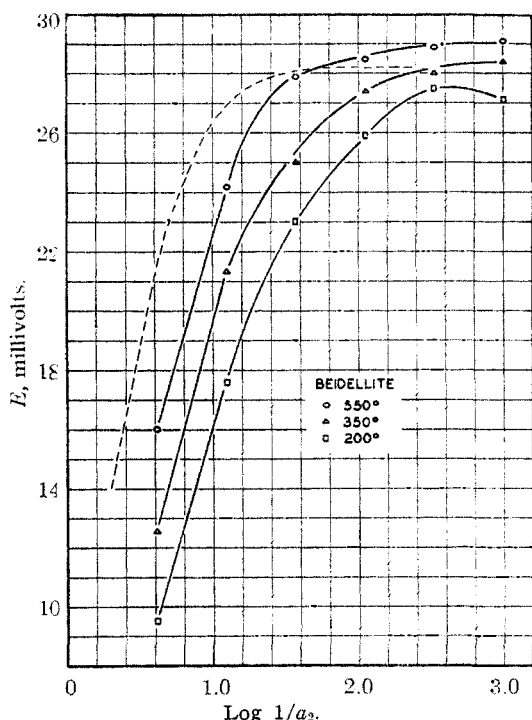


Fig. 1.—Experimental curves obtained with electro-dialyzed beidellite membranes dried to various temperatures using potassium chloride solutions with an activity ratio  $a_1/a_2 = 3$ . The broken line is the theoretical curve for  $U_c/U_A = 1$  and  $A = 1$ ,  $A$  being the effective charge per unit volume of the membrane.

It will be seen from Fig. 1 that the beidellite membranes give curves lying farther to the right than those previously obtained with 490° montmorillonite.<sup>3</sup> This indicates a smaller ionic charge

TABLE I  
CHARACTERISTICS OF CLAY MEMBRANES PREPARED IN VARIOUS WAYS

Ex-change-able cation	Temp. of pre-treatment, °C.	Approximate resistance (megohms)		Cations to which sensitive
		Wet	Dry <sup>a</sup>	
Montmorillonite				
H	350	0.005-011	200	Mono-, divalent
H	490	1-10	400	Monovalent
H	550	Very low	...	None
Beidellite				
H	110	0.005	3	Mono-, di-, trivalent
H	600	0.012	15-45	
H	750	0.015		
H	900	>1000		

<sup>a</sup> Dry indicates an atmosphere of 50% relative humidity.

per unit volume, approximately 0.5 for the 550° beidellite whereas the 490° montmorillonite was 1.0. This is probably to be accounted for by the lower exchange capacity of the beidellite. In consequence, agreement within 1 millivolt with the Nernst equation can only be expected for solutions less concentrated than  $N/30$ . Even with this limitation the beidellite membranes are to be preferred over the 350 or 490° montmorillonite membranes where both can be used for the same ion. The beidellite membranes come to equilibrium with fresh solutions much more rapidly (within a few minutes, instead of after several hours), the initial asymmetry potentials disappear more rapidly on soaking, and the individual differences between membranes are smaller. This last point can perhaps best be seen by a comparison of typical numerical results for montmorillonite and beidellite membranes (Table II).

TABLE II  
COMPARISON OF INDIVIDUAL POTENTIALS FOR 350° MONTMORILLONITE AND 550° BEIDELLITE MEMBRANES IN SODIUM CHLORIDE SOLUTIONS AT 25°. THEORETICAL NERNST POTENTIAL IS 28.2 MILLIVOLTS

Activity ratio $a_1/a_2$	350° Montmorillonite				
	1	2	3	4	5
0.7101/0.2367	16.2	15.3	18.1	17.1	16.4
.2367/.0789	23.0	20.5	24.2	22.9	22.0
.0789/.0263	27.1	26.5	27.0	27.7	27.0
.0263/.0088	29.0	28.1	28.4	29.2	28.9
.0088/.0029	26.5	26.5	27.3	27.1	26.7
.0029/.0010	27.6	27.2	27.1	27.6	27.3
550° Beidellite					
0.7107/0.2367	16.3	16.0	15.8	16.7	16.6
.2367/.0789	23.4	23.9	24.8	25.5	25.6
.0789/.0263	27.5	27.2	27.6	27.6	27.5
.0263/.0088	28.3	28.2	28.8	28.6	28.5
.0088/.0029	28.4	28.3	28.4	28.3	28.3
.0029/.0010	27.9	27.7	28.5	28.0	28.4

In Fig. 2 the results for sodium chloride solutions are presented, using the same 1:3 ratio of cationic activities as for potassium chloride in Fig. 1. It can be seen that the 550° beidellite membranes are superior both to the 750° beidellite and the 350° montmorillonite membranes.

**Comparison of Different Sodium Salts.**—Table III gives the mean potentials obtained for beidellite membranes with sodium salts. At least six membranes were used in each case. The standard solution used throughout was 0.1 *N* sodium chloride which gives an activity  $a_1$  of 0.0789.

TABLE III

MEAN POTENTIALS OBTAINED WITH BEIDELLITE MEMBRANES IN SODIUM SALT SOLUTIONS ( $a_1 = 0.0789 \text{ Na}^+$ )

Temp. of pretreatment, °C.	Salt	Activity of $\text{Na}^+$ in $a_2$	Observed potential, mv.	Calcd. potential, mv.
550	NaCl	0.0266	27.5	27.9
	NaCl	.00864	56.8	56.8
	NaCl	.00292	83.7	84.7
	NaCl	.00091	111.4	113.0
630	NaCl	.0263	27.5	28.2
	NaCl	.00877	56.1	56.4
	NaCl	.00292	83.7	84.7
	NaCl	.00097	111.2	112.9
550	$\text{Na}_2\text{SO}_4$	.0386	18.8	18.4
	$\text{Na}_2\text{SO}_4$	.00915	55.5	55.4
	$\text{Na}_2\text{SO}_4$	.00458	72.9	73.2
630	$\text{Na}_2\text{SO}_4$	.0386	18.5	18.4
	$\text{Na}_2\text{SO}_4$	.00915	55.2	55.4
	$\text{Na}_2\text{SO}_4$	.00458	72.9	73.2
550	Na citrate	.0395	21.2	17.8
	Na citrate	.00875	58.3	56.5
	Na citrate	.00452	75.4	73.5
630	Na citrate	.0395	21.0	17.8
	Na citrate	.00875	57.6	56.5
	Na citrate	.00452	74.6	73.5
610	$\text{Na}_4\text{Fe}(\text{CN})_6$	.0410	16.8	16.8
	$\text{Na}_4\text{Fe}(\text{CN})_6$	.00916	55.1	55.9
	$\text{Na}_4\text{Fe}(\text{CN})_6$	.00475	71.2	72.1

Excellent agreement is found except in the case of the more concentrated solutions of sodium citrate where the experimental values are consistently high. It does not appear that this can be due to the high valence of the anion, since ferrocyanide gives almost perfect values. However, it has been shown<sup>7</sup> that sodium citrate solutions give low osmotic pressures at concentrations above 25 millimoles per liter. It seems logical, therefore, to assume that the activity of part of the sodium is reduced by some kind of complex formation.

(7) Adie, *J. Chem. Soc.*, **59**, 344 (1891).

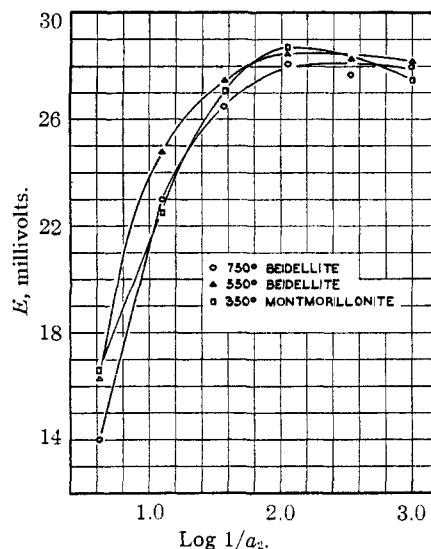


Fig. 2.—Experimental curves obtained with different membranes using sodium chloride solutions with an activity ratio  $a_1/a_2 = 3$ .

**The Behavior of Cationic Mixtures.**—In Part I<sup>3</sup> it was pointed out that the potentials established when a potassium salt is present on one side of the membrane and a sodium salt on the other may depend on the relative mobilities of the cations as well as on their activities. The exact relationship may be derived in two ways.

(1) In the range over which the membrane gives Nernst potentials for single salts, we can start out from the general Henderson equation for a liquid junction potential and incorporate the simplifying assumption that the mobility of the anions is negligible compared with that of the cations. For instance, with potassium chloride on one side of the membrane and a mixture of potassium and sodium chlorides on the other, the potential is given by the equation

$$E = \frac{RT}{F} \ln \frac{U_K a'_K}{U_K a''_K + U_{Na} a''_{Na}} \quad (1)$$

If sodium chloride alone is present on one side of the membrane this reduces to the form

$$E = \frac{RT}{F} \ln \frac{U_K a'_K}{U_{Na} a''_{Na}} \quad (2)$$

Here the mobilities, represented by  $U_K$  and  $U_{Na}$  are those of the respective cations within the membrane. These values are not necessarily those of the cations in pure water.

Using the Henderson equation as the starting point, more general cases can be dealt with. If the cation  $x$  accompanying potassium on the one side of the membrane has a valence  $n$ , then the equation becomes

$$E = \frac{RT}{F} \frac{U_K a''_K + U_x a''_x - U_K a'_K}{U_K a''_K + n U_x a''_x - U_K a'_K} \ln \frac{U_K a'_K}{U_K a''_K + n U_x a''_x} \quad (3)$$

and when there is only the polyvalent cation  $x$  on one side and potassium on the other, this reduces to

$$E = \frac{RT}{F} \frac{U_x a''_x - U_K a'_K}{n U_x a''_x - U_K a'_K} \ln \frac{U_K a'_K}{n U_x a''_x} \quad (4)$$

(2) An expression covering also the higher concentrations for which Nernst potential is not attained has been derived for binary salts by Meyer and Sievers.<sup>8</sup> In this equation the effective charge  $A$  of the membrane and the solubilities of the two salts in the membrane are additional variables. For those cases in which  $A$  is large compared with the cationic activities and in absence of solubility changes this equation reduces to the same form as (2) above.

These equations lend themselves readily to experimental verification and by their use the ratios of the mobilities of the cations within the membrane may be determined. For monovalent ions the most accurate procedure is to determine the mobility ratio under the conditions of Eq. 2 with one electrolyte on each side of the membrane. The validity of Eq. 1 may then be tested with mixtures using the determined value of the mobility ratio. It will be seen from Eq. 4 that for polyvalent cations the conditions are less favorable. However, if the activity of the monovalent ion is small compared with that of the polyvalent ion a satisfactory value of the mobility ratio should be obtained.

In Table IV, several determinations with monovalent cations are assembled. From the potentials the mobility ratios were calculated and

TABLE IV  
DETERMINATION OF CATIONIC MOBILITY RATIOS WITHIN THE MEMBRANES

Mem- brane temp., °C.	Cations and activities		Poten- tial, mv.	Mobility ratio $U_x/U_1$
	Inside $a_1$	Outside $a_2$		
Beidellite				
600	K <sup>+</sup> 0.0270	Na <sup>+</sup> 0.0263	26.0	0.373
550	K <sup>+</sup> .0270	Na <sup>+</sup> .0263	26.1	.371
630	K <sup>+</sup> .0270	Na <sup>+</sup> .0263	24.5	.395
600	K <sup>+</sup> .0270	Na <sup>+</sup> .00877	53.7	.372
600	K <sup>+</sup> .0270	Na <sup>+</sup> .00292	78.2	.430
600	K <sup>+</sup> .0090	Na <sup>+</sup> .00877	25.4	.395
600	K <sup>+</sup> .0090	Na <sup>+</sup> .00292	51.5	.409
	Mean value $U_{Na}/U_K =$			.392
610	Na <sup>+</sup> .00877	H <sup>+</sup> .000068	72.4	.130
610	Na <sup>+</sup> .00877	H <sup>+</sup> .000135	55.4	.134
610	Na <sup>+</sup> .00877	H <sup>+</sup> .000851	5.0	.119
	Mean value $U_{Na}/U_H =$			.128

(8) Meyer and Sievers, *Helv. Chim. Acta*, **19**, 649 (1936).

these display reasonable constancy. Some variation of the mobility ratio with concentration might be expected. However, in Table IV the range covered runs only from about  $N/30$  downward and the figures show no definite trend. In pure aqueous solutions also the variation in transport number is small for concentrations below  $N/20$ .

Values of the mobility ratios obtained are used in Table V in order to compare the experimental with the theoretical potentials.

The use of the mean mobility ratios  $U_{Na}/U_K$  and  $U_{Na}/U_H$  lead to excellent agreement between the observed and calculated potentials when measurements are made with a pure salt solution on one side of the membrane and a mixture on the other.

TABLE V  
POTENTIALS OBTAINED WITH MIXTURES OF CHLORIDES OF MONOVALENT CATIONS, BEIDELLITE MEMBRANES

Mem- brane temp., °C.	Cations and activities	Potential, mv.	
		Ob- served	Calcd.
600	K <sup>+</sup> 0.0270 K <sup>+</sup> 0.00095 Na <sup>+</sup> 0.00095	76.9	77.3
550	K <sup>+</sup> .0270 K <sup>+</sup> .00095 Na <sup>+</sup> .00095	77.0	77.3
630	K <sup>+</sup> .0270 K <sup>+</sup> .00095 Na <sup>+</sup> .00095	76.6	77.3
630	K <sup>+</sup> .0270 K <sup>+</sup> .00884 Na <sup>+</sup> .00443	23.4	24.0
630	K <sup>+</sup> .0270 K <sup>+</sup> .00442 Na <sup>+</sup> .00877	31.5	31.5
610	Na <sup>+</sup> .00877 Na <sup>+</sup> .00097 H <sup>+</sup> .000068	46.9	45.3
610	Na <sup>+</sup> .0877 Na <sup>+</sup> .00097 H <sup>+</sup> .000891	3.5	2.8

It is evident from the foregoing that the simple type of Nernst formula used in calculating the clay titration curves in Parts II and IV is inadequate. However, the difference in actual result between it and the correct expression involving the mobility ratio is negligible, except for those first additions of potassium or ammonium hydroxide which bring the clay to a pH below 4.5.

**Acknowledgment.**—The authors are indebted to the Research Council of the University of Missouri for a grant-in-aid which has made this work possible.

### Summary

1. Clay membranes have been prepared which are sensitive only to monovalent cations (H-montmorillonite 490°); to monovalent and divalent cations (H-montmorillonite 350°); and to mono, di and trivalent cations (H-beidellite 600°).

2. For sodium estimations, beidellite membranes gave excellent reproducibility. The potentials obtained with solutions less concentrated than 0.03  $N$  were within 1 millivolt of those calculated using the Nernst equation.

3. Sodium chloride, sulfate and ferrocyanide gave practically the theoretical potentials whereas low values were obtained with sodium citrate. This is ascribed to complex formation.

4. The behavior of mixtures of cations can be predicted and the mobility ratios of the cations

within the clay membranes have been determined experimentally in certain cases. Using these values, the experimental and theoretical potentials for mixtures of cations are found to be in good agreement.

COLUMBIA, MISSOURI

RECEIVED MAY 4, 1942

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

## Crystal-Chemical Studies of the Alums. IV. Coefficients of Linear Thermal Expansion<sup>1</sup>

BY HAROLD P. KLUG AND LEROY ALEXANDER

In the systematic study of the crystal chemistry of the alums now in progress in this Laboratory, as many as possible of the physical and chemical properties of their crystals are being investigated. The only thermal expansion data on the commoner alums seem to be the somewhat uncertain results of Spring,<sup>2-4</sup> who determined the change in density with temperature for several alums, and calculated the volume changes therefrom. Spring concluded that his earlier values<sup>2,3</sup> were vitiated by partial dehydration of the alums and repeated the measurements.<sup>4</sup> He was unwilling, however, to claim that his final results solely expressed the volume change brought about by thermal expansion because of the possibility of some dissociation of the hydrates with increasing temperature.

In view of the uncertainty of these results, and of the ease with which such measurements can be made by means of X-ray diffraction, it seemed desirable to determine the coefficients of expansion of a few alums by the X-ray technique. Since the characteristic powder diffraction pattern of the alums is particularly sensitive to the effects of dehydration,<sup>1</sup> the X-ray method presents an important advantage over the pycnometric and dilatometric methods. This communication presents the results of such measurements, for the approximate temperature range 20 to 50°, on the following alums:  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{TlAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  and  $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

### Experimental

The potassium and ammonium alums used were from lots prepared for a previous study.<sup>5</sup> The

- (1) Paper III, *THIS JOURNAL*, **62**, 2993 (1940).
- (2) Spring, *Bull. classe sci. acad. roy. belg.*, [3] **3**, 331 (1882).
- (3) Spring, *Ber.*, **15**, 1254 (1882).
- (4) Spring, *ibid.*, **17**, 408 (1884).
- (5) Klug and Alexander, *THIS JOURNAL*, **62**, 1492 (1940).

thallium alum was a sample prepared by Dr. N. O. Smith,<sup>6</sup> and presented by Professor J. E. Ricci for an earlier study.<sup>1</sup> The ammonium chrome alum was the reagent grade salt used without further purification.

The experimental technique followed was that of Straumanis and co-workers,<sup>7</sup> which involves precision determination of the lattice constants at two different temperatures by thermostating the camera. Details of the thermostat and X-ray technique have been described previously.<sup>5,7</sup> FeK radiation was used throughout the study except in the case of the chrome alum where CrK radiation was used.

### Results

The mean coefficient of linear thermal expansion  $\alpha$ , the average increase per unit length per degree centigrade, can be obtained from the expression

$$\alpha = \frac{a_{t_2} - a_{t_1}}{a_{t_1}(t_2 - t_1)}$$

where  $a_t$  is the lattice constant at the corresponding temperature  $t$ .

The results of the study are tabulated in Table I. For each alum the temperatures and corresponding lattice constants of the separate determinations are listed together with the mean value of  $\alpha \cdot 10^6$  obtained by using all possible combinations of lattice constants separated by at least a 25° interval. The error is expressed as the probable error of the mean.

Spring gives no data which can be compared directly with the values of  $\alpha$  in Table I. When his best data<sup>4</sup> are recalculated, they lead to the follow-

- (6) Hill, Smith and Ricci, *ibid.*, **62**, 858 (1940).
- (7) Straumanis, Ievins and Karlsons, *Z. anorg. allgem. Chem.*, **238**, 175 (1938).