

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

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[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 Expansion¹

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,²⁻⁴ who determined the change in density with temperature for several alums, and calculated the volume changes therefrom. Spring concluded that his earlier values^{2,3} were vitiated by partial dehydration of the alums and repeated the measurements.⁴ 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,¹ 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.⁵ The

- (1) Paper 111, *THIS JOURNAL*, **62**, 2993 (1940).
- (2) Spring, *Bull. classe sci. acad. roy. belg.*, [3] **3**, 331 (1882).
- (3) Spring, *Ber.*, **15**, 1234 (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,⁶ and presented by Professor J. E. Ricci for an earlier study.¹ The ammonium chrome alum was the reagent grade salt used without further purification.

The experimental technique followed was that of Straumanis and co-workers,⁷ 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.^{5,7} 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 α , the average increase per unit length per degree centigrade, can be obtained from the expression

$$\alpha = \frac{a_2 - a_1}{a_1(t_2 - t_1)}$$

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 α in Table I. When his best data⁴ 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 (1933).

TABLE I
LATTICE CONSTANTS AND COEFFICIENTS OF EXPANSION OF THE ALUMS BETWEEN 20–50°

KAl(SO ₄) ₂ ·12H ₂ O		NH ₄ Al(SO ₄) ₂ ·12H ₂ O		TlAl(SO ₄) ₂ ·12H ₂ O		NH ₄ Cr(SO ₄) ₂ ·12H ₂ O	
Temp., °C.	a, Å.	Temp., °C.	a, Å.	Temp., °C.	a, Å.	Temp., °C.	a, Å.
19.3	12.1333	19.2	12.2141	18.8	12.2047	22.1	12.2501
19.9	12.1335	19.4	12.2142	19.0	12.2045	25.0	12.2510
25.0	12.1336	19.5	12.2148	19.1	12.2040	50.5	12.2539
50.5	12.1372	50.4	12.2180	25.0	12.2050	51.1	12.2543
51.1	12.1378	50.8	12.2181	50.6	12.2095		
52.2	12.1373	51.4	12.2179	51.1	12.2093		
$\alpha \cdot 10^6 = 11.0 \pm 0.3$		$\alpha \cdot 10^6 = 9.5 \pm 0.2$		$\alpha \cdot 10^6 = 13.1 \pm 0.3$		$\alpha \cdot 10^6 = 10.6 \pm 0.4$	

ing values of $\alpha \cdot 10^6$ for the first three alums listed above: 3.3, 6.8 and 18.3, respectively. These values are of the right order of magnitude but, otherwise, are in poor agreement with the X-ray values. No data are available for comparison with the result for ammonium chrome alum.

Potassium chrome alum was also studied at this same time but the inability, after numerous attempts, to get photographs in the vicinity of 50° without dehydration led to its abandonment.

The authors wish to express their thanks and appreciation to Dr. N. O. Smith and Professor J. E. Ricci for the sample of thallium alum. They

also wish to acknowledge with gratitude a grant from the Graduate School of the University of Minnesota under which this study was carried out.

Summary

The linear thermal expansion coefficients α for several alums have been measured for the approximate range, 20–50°, by means of X-ray diffraction. The values of $\alpha \cdot 10^6$ observed are as follows: potassium alum, 11.0 \pm 0.3; ammonium alum, 9.5 \pm 0.2; thallium alum, 13.1 \pm 0.3; and ammonium chrome alum, 10.6 \pm 0.4.

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The Vapor Phase Photo Decomposition of Methyl Formate

BY DAVID H. VOLMAN¹

Recently, experiments on the photolysis of methyl formate have been reported by Royal and Rollefson.² Experiments on this same problem had been in progress in this Laboratory. The results for the photolysis products in this investigation are in substantial agreement with those given by Royal and Rollefson. In addition, data on the determination of methanol in the reaction products, and an approximate evaluation of the quantum yield for the reaction were obtained.

In a subsequent paper on the photolysis of methyl acetate, Roth and Rollefson³ have given data on the determination of methanol as a photolysis product by oxidizing the alcohol to formaldehyde and treating with Schiff reagent. However, they were unable to analyze for the small amounts of methanol usually obtained in the decomposition runs, and were forced to obtain

comparatively large amounts of decomposition products by carrying out the reaction in a three-liter bulb. The method given below using a Grignard reagent suffices for the small amounts usually obtained and enables analyses to be made for all of the decomposition experiments conducted.

Experimental Method

The apparatus employed was essentially the same as already reported.⁴ The source of radiation was an Hanovia Alpine mercury lamp. Quantum yields were determined approximately by using monochloroacetic acid as an actinometer in a manner previously described^{4,5} using the reliable value for the hydrolysis quantum yield given by Smith, Leighton and Leighton.⁶

Methyl formate was synthesized by allowing formic acid and methanol to react in the presence

(1) On leave of absence. Present address: The Technological Institute, Northwestern University, Evanston, Illinois.

(2) Royal and Rollefson, *THIS JOURNAL*, **63**, 1521 (1941).

(3) Roth and Rollefson, *ibid.*, **64**, 490 (1942).

(4) Volman, *ibid.*, **63**, 2000 (1941).

(5) Weizmann, Bergmann and Hirshberg, *ibid.*, **58**, 1675 (1936).

(6) Smith, Leighton and Leighton, *ibid.*, **61**, 2299 (1939).