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

Crystal-Chemical Studies of the Alums. V. The Gallium Alums[1,2]

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The fact that gallium forms alums has been known since 1877 when de Boisbaudran, its discoverer, prepared the ammonium alum.[4] Soret[5] also prepared the ammonium alum and in addition described the preparation of the potassium, rubidium and cesium alums, while the thallous alum was first studied by de Boisbaudran.[4] Although the ability of the elements of Group III to form alums decreases from the top of the group to the bottom, gallium is sufficiently active in this respect that the above compounds are readily obtained and have sufficient stability for further study.

The ultimate goal in the systematic study of the alums in progress in this Laboratory is the examination of most of the known alums, in order to ascertain whether other alum structures exist, in addition to the three described by Lipson,[6] and to learn, if possible, the conditions which determine structure type. In the present communication the results of a study of the lattice constants, densities (from X-ray data), and structure types of the gallium alums are reported.

Experimental

The various alums were prepared by mixing solutions of the stoichiometric quantities of gallic sulfate and the appropriate univalent sulfate, and allowing the resulting solutions to evaporate until crystals formed. The gallic sulfate was prepared from a pure sample of gallic hydroxide obtained by the following purification treatment. Proceeding according to Bates[7] the commercial metal was dissolved in sulfuric acid and the resulting solution treated with hydrogen sulfide to precipitate any metals of Group II. Zinc was then removed, with some loss of gallium, by the repeated precipitation of gallic hydroxide with slight excess of ammonium hydroxide. Next, iron and indium were separated from the gallium by means of sodium hydroxide as described by Swift.[8] Finally the separation from aluminum was achieved by extracting the gallium chloride from the mixture of chlorides with ether saturated with hydrogen chloride following the scheme of Noyes and Bray.[9] The gallic chloride thus obtained was transformed to the hydroxide and thence to the sulfate.

After preparation the composition of each alum was checked. Duplicate samples were analyzed for gallium by precipitation of the hydroxide with ammonium acid sulfite and subsequent ignition, as described by Hillebrand and Lundell.[10]

The X-ray technique was the same as described earlier,[11] except that a temperature regulator of the vapor sensitive type was used in the thermostat to achieve better temperature control. FeK radiation was used with $\lambda_{\alpha_1} = 1932.08$ X. U.[12] The densities were calculated in the usual way from the X-ray data on the basis of four molecules of the dodecahydrate formula per unit cell and the value 6.06×10^{23} for Avogadro's number.[13]

The probable structure type was determined by a slightly more precise modification of the technique described by Lipson.[14] The intensities of the prism planes, (210), (230), (420), (610) and (620), were visually estimated using a calibrated scale. These were then divided by the Lorentz and polarization factors, and the square root of the quotient taken, to obtain the observed structure factors for the planes. These multiplied by a suitable constant, were compared with calculated structure factors for the same planes, first based on the assumption of the parameters of potassium aluminum alum[15] (α structure) and then on the assumption of the parameters for cesium aluminum alum[6] (β structure), to decide the structure type.

Results

In Table I the probable structure types and the precise lattice constants of the gallium alums are tabulated. The lattice constants are given in terms of kX. units[16] and are believed to be good to ±0.001 kX. U. There are no previous lattice constant data available on any of these alums for comparison.

TABLE I

STRUCTURE TYPES AND LATTICE CONSTANTS OF THE GALLIUM ALUMS

Alum	Probable structure type	Lattice constant in kX. U. at 25 ± 0.1°
$NH_4Ga(SO_4)_2 \cdot 12H_2O$	α	12.243 ± 0.001
$KGa(SO_4)_2 \cdot 12H_2O$	α	12.198 ± 0.001
$RbGa(SO_4)_2 \cdot 12H_2O$	α	12.245 ± 0.001
$CsGa(SO_4)_2 \cdot 12H_2O$	β	12.377 ± 0.001
$TlGa(SO_4)_2 \cdot 12H_2O$	β	12.233 ± 0.001

TABLE II

DENSITY DATA FOR THE GALLIUM ALUMS

Alum	Density at 25° (from X-ray data)	Reported density 20°/4°[a]
NH_4	1.784	1.77
K	1.879	1.895
Rb	2.025	1.962
Cs	2.126	2.113
Tl	2.460	2.477

[a] "International Critical Tables," Vol. I.

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[1] Paper IV in this series appeared in THIS JOURNAL, **64**, 1819 (1942).

[2] Abstracted in part from a thesis by G. L. Kieffer, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the M.S. degree, May, 1943.

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[4] de Boisbaudran, *Chem. News*, **35**, 167 (1877); *Ann. chim. phys.*, [5] **10**, 126 (1877).

[5] Soret, *Arch. Sciences Genève*, [3] **14**, 96 (1885); [3] **20**, 530 (1888).

[6] Lipson, *Proc. Roy. Soc.* (London), **151A**, 347 (1935).

[7] Bates, *Sci. Papers Bur. Standards*, No. 371, **16**, 45 (1920).

[8] Swift, THIS JOURNAL, **46**, 2375 (1924).

[9] Noyes and Bray, "Qualitative Analysis of the Rarer Elements," The Macmillan Co., New York, N. Y., 1927, p. 160.

[10] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 388.

[11] Klug, THIS JOURNAL, **62**, 1492 (1940).

[12] "International Tables for the Determination of Crystal Structure," Gebrüder Borntraeger, Berlin, 1935, Vol. II, p. 586.

[13] In this connection note Lipson and Riley, *Nature*, **151**, 250 (1943).

[14] Lipson, *Phil. Mag.*, **19**, 887 (1935).

[15] Lipson and Beevers, *Proc. Roy. Soc.* (London), **148A**, 664 (1935).

[16] See Wilson, *Nature*, **151**, 562 (1943). In this connection it should be pointed out that all earlier studies in this series have been made with X-rays referred to the Siegbahn scale. The results then are really in kX. units rather than in Å. units as reported.

In Table II the densities of the gallium alums calculated from the X-ray data, together with previously reported density data, are tabulated.

It is interesting to compare the structure types and lattice constants of the alums with those of the aluminum and chrome alums.[17] The ammonium and potassium alums of each have the α structure, while the three cesium alums have the β structure. With rubidium the univalent ion, substitution of Cr^{+3} for Al^{+3} results in a change from α to β structure, but with Ga^{+3} the structure is again α. Among the thallous alums all are β except the aluminum alum. On the basis of size alone Ga^{+3} and Cr^{+3} would be expected to act alike in replacing Al^{+3} since they are almost identical in size. Pauling[18] reports for the radii of Ga^{+3}, Cr^{+3} and Al^{+3}, values of 0.62, 0.64 and 0.50 Å., respectively. It is thus evident that the factors determining structure type are rather complex, and sufficient data are not yet available for their description and identification.

The increase in the lattice constant, Δa_0, on substituting Ga^{+3} for Al^{+3} is as follows for the various alums: $NH_4 = 0.029$, $K = 0.065$, $Rb = 0.025$, $Cs = 0.047$, and $Tl = 0.026$ kX. U. Thus Δa_0 for the gallium alums is less constant than for the chrome alums,[17] but its average value is exactly the same, 0.038 kX. U. The variations from the average in both series of alums are without doubt real, since they are much larger than the estimated error ± 0.001 kX. U. in determining a_0, and indicate the complexity of the forces involved as compared with the simple ionic lattices where distances are additive and substitution of a larger cation will bring about a corresponding increase in lattice constants.

Summary

1. Lattice constants for a series of gallium alums have been determined at $25 \pm 0.1°$.

2. The densities of these alums at 25° have been calculated from the X-ray data.

3. The probable structure types of the alums have been determined. All of the gallium alums investigated have the α structure except those of cesium and thallium which possess the β structure.

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(17) Klug, THIS JOURNAL, **62**, 2992 (1940).

(18) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1st ed., 1939, pp. 326, 330.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Osmotic Activity of Colloidal Electrolytes

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Introduction

In moderately concentrated solutions of colloidal electrolytes, the lowering of freezing point or of vapor pressure is perhaps a fifth of that expected for an electrolyte, whereas the conductivity may be halved. The existence of colloidal aggregates is necessitated by the low osmotic activity, although the conductivity is at least twice that expected for the osmotically active ion. In 1920, McBain and Salmon[1] interpreted the data then available in terms of the highly conducting ionic micelle and the far less highly charged and conducting lamellar aggregate, unfortunately termed the "neutral micelle." According to the measurements of M. E. Laing McBain,[2] the latter conducts only about seven per cent. as well as an equivalent amount of fully dissociated ions. Its existence and structure have been confirmed by X-ray examination of the solutions of soaps and other detergents.[3-6] The high conductivity of the solution and the comparatively low migration number necessitated the introduction of two types of micelle, the poorly conducting lamellar micelles and the highly conducting small or ionic micelles.

Prior to 1939, only conductivity had been measured in the very dilute solutions where the transition from an ordinary uni-univalent electrolyte to a colloidal electrolyte occurs. The dew-point lowering method employed so successfully by McBain and Salmon at higher concentrations is entirely too inaccurate; even ordinary freezing point technique is not suitable. Recently, however, McBain and Johnston[7] and McBain and Bolduan[8] have studied freezing points in a precise apparatus modelled after that of Scatchard,[9] with which solutions as dilute as 0.001 *m* may be measured with acceptable accuracy. The purpose of the present paper is to supplement these freezing point data, and to collect and to correlate the now fairly extensive experimental material on this subject.

Experimental Method

The Scatchard apparatus was used and calibrated with the standard values given by Scat-

(1) J. W. McBain and C. S. Salmon, THIS JOURNAL, **42**, 426 (1920).

(2) M. E. Laing, *J. Phys. Chem.*, **28**, 673 (1924); M. E. Laing McBain, *Trans. Faraday Soc.*, **31**, 153 (1935); *J. Phys. Chem.*, **47**, (1943).

(3) Hess and Gundermann, *Ber.*, **70B**, 1800 (1937).

(4) Hess, Philippoff and Kiessig, *Kolloid Z.*, **88**, 40 (1939).

(5) Stauff, *ibid.*, **89**, 224 (1939); **96**, 244 (1941); *Naturwissenschaften*, **27**, 213 (1939).

(6) Kiessig and Philippoff, *ibid.*, **27**, 593 (1939).

(7) McBain and Johnston, *Proc. Roy. Soc.* (London), **181A**, 119 (1942).

(8) McBain and Bolduan, *J. Phys. Chem.*, **47**, 94 (1943).

(9) Scatchard, Jones and Prentiss, THIS JOURNAL, **54**, 2676 (1932).