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The Formula of Ammonium Paramolybdate

BY J. H. STURDIVANT

In 1917 Rosenheim[1] advocated for the paramolybdates the formula $R_5H_5[H_2(MoO_4)_6]$. The previously accepted formula had described the compounds as heptamolybdates, $R_6Mo_7O_{24}\cdot 4H_2O$. Analytical methods were unable to decide between the two formulas until recently, when the heptamolybdate formula was reaffirmed on the basis of analyses of mixed paramolybdates of ammonia and triethanolamine.[2]

In the present paper additional evidence for the heptamolybdate formula will be described, based on X-ray measurement of the lattice constants and a determination of the density of crystalline ammonium paramolybdate.[3]

Cooling a saturated ammoniacal solution of Powers–Weightman–Rosengarten ammonium molybdate, C. P. grade, produced crystals in the form of rhomboidal plates about 2 mm. × 1 mm. × $^1/_3$ mm. Forms observed, in the notation of Groth,[4] were $b(010)$, $o(111)_G$, $n(310)_G$, $m(110)_G$. As foreshadowed by the habit of the crystals, the X-ray investigation required a new assignment of axes, which will be used throughout this paper. The new axis $\mathbf{a}$ is taken parallel to $[10\bar{1}]_G$ of Groth, and the new axis $\mathbf{c}$ parallel to $\mathbf{c}_G$ of Groth. From the monoclinic angle 91°12′ given by Groth and the axial ratios of Groth, the value β = 115°59′ is calculated. From direct goniometric measurements on the plates used in this investigation, β was found to be 116°0′ ± 4′. Monochromatic X-ray photographs were prepared by oscillating a crystal through small angles on each side of the primary beam to give selected orders of reflection from the a, b and c planes. The cylindrical camera of 5 cm. nominal radius was calibrated by the use of calcite as a standard crystal with the grating space given by Siegbahn.[5] Film shrinkage was allowed for by marks imposed on the film before development. The radiation was from a copper target. The following spacings[6] were obtained at about 24°:

$d_{(100)}$ = 7.534 ± 0.010 Å. from measurements of (100), (200), (300).
$d_{(010)}$ = 36.125 ± 0.008 Å. from measurement of (0·36·0).
$d_{(001)}$ = 9.405 ± 0.005 Å. from measurement of (0·0·10).

Layer line measurements and data from a Laue photograph proved that the corresponding axes describe a true unit of structure of minimum volume, and the unit was further shown by Laue data to be simple. Groth describes ammonium paramolybdate as monoclinic prismatic. Two Laue photographs taken with the X-ray beam approximately parallel to $\mathbf{a}$ indicated that interferences $(h0l)$ with l odd do not occur. On oscillation photographs interferences $(0n0)$ with n odd were absent. The space-group is therefore $C_{2h}^5 - P2_1/c$.

The density was measured of a 7-g. sample of the original commercial product, ground to pass through a 150-mesh sieve, and weighed in a pycnometer filled with carbon tetrachloride. During addition of the carbon tetrachloride the air was exhausted from the pycnometer and powder. The density was found to be 2.871 ± 0.003 at 25°.

The weight of a mole of unit cells is $0.6064 \times 10^{24} \times \rho \times d_{(100)} \times d_{(010)} \times d_{(001)} \times (\sin\beta)^{-1} = 4958 \pm 20$. The formula $(NH_4)_5H_5[H_2(MoO_4)_6]$ corresponds to a molecular weight of 1057; this number is contained 4.7 times in 4958; and 4.7 differs from an integer by more than the experimental error. On the other hand, four molecules of the heptamolybdate formula in the unit cell would give a weight equal to 1236.3 × 4 = 4945. The conclusion is therefore reached that the formula of ammonium paramolybdate is $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

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[1] A. Rosenheim, M. Pieck and J. Pinsker, *Z. anorg. allgem. Chem.*, **96**, 139–181 (1916).

[2] F. Garelli and A. Tettamanzi, *C. A.*, **29**, 7846^6 (1935); **30**, 4114^4 (1936).

[3] Molecular weight determinations by the methods of X-ray crystallography have been reported previously by D. Crowfoot, *Chemistry and Industry*, **54**, 568 (1935), and by D. Crowfoot and H. Jensen, THIS JOURNAL, **58**, 2018 (1936).

[4] P. Groth, "Chemische Kristallographie," W. Engelmann, Leipzig, 1908, Teil II, p. 603.

[5] M. Siegbahn, "Spektroskopie d. Röntgenstrahlen," Verlag von J. Springer, Berlin, 1931, pp. 44–45.

[6] The fundamental translations calculated from these spacings and β = 116°0′ are a = 8.382 Å., $b = d_{(010)}$, c = 10.464 Å. Thence the axial ratios $a_G:b_G:c_G$ = 0.6258:1:0.2897 are calculated. Groth gives, however, $a_G:b_G:c_G$ = 0.6297:1:0.2936. The disagreement is not surprising in view of the generally poor quality of the faces of ammonium molybdate crystals, which is reflected, for example, in the detailed measurements reported by P. Rossoni, *Atti soc. toscana sci. nat., proc. verb.*, **42**, 10–19 (1933). The nature of the imperfections, particularly the development of vicinal faces in the zone of [001], is, however, not such as to diminish seriously the accuracy of direct measurement of β.

ing for suggesting the study of ammonium paramolybdate.

Summary

The lattice constants, space groups and density of crystalline ammonium paramolybdate were determined. From the weight of the unit of structure it is concluded that the compound is a heptamolybdate, with the formula $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Solubilities of Barium and Strontium Carbonates in Aqueous Solutions of Some Alkali Chlorides

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Object of the Investigation

A number of investigations dealing with the change in solubilities of the alkaline earth carbonates in aqueous salt solutions have been recorded. In each case an increase in solubility was noted. Muir[1] studied the solubility of calcium carbonate in sodium chloride solutions. Cameron and Robinson,[2] Cantoni and Goguelia,[3] and Dubrisay and François[4] studied the influence of potassium chloride upon the solubility of calcium carbonate and the last-named investigators also studied the influence of potassium chloride upon the barium carbonate solubility. De Coninck and Arzalier[5] briefly mention their study of the solubility of strontium carbonate in the presence of potassium chloride. In no case, however, was the study made with the view of determining the activity of these alkaline earth carbonates by the method outlined by Lewis and Randall.[6]

The purpose of this investigation, hence, was the determination of the influence of increasing concentrations of lithium, sodium, and potassium chlorides upon the solubilities of the normal carbonates of barium and strontium. It was hoped that the data obtained would yield information of value regarding the activities of these carbonates.

Previous Investigations

The solubility of barium carbonate in pure water has been reported[7] at various temperatures; McCoy and Smith's value at 25°, as calculated from their solubility product, is 0.90×10^{-4} g. moles/1000 g. of water. The solubility of strontium carbonate is also recorded by several investigators.[8] McCoy and Smith's value at 25° is 0.396×10^{-4} g.-moles/1000 g. water.

Experimental Methods

The method of this investigation consisted of saturating solutions of lithium, sodium, and potassium chlorides at different concentrations (approx. 0.02, 0.06, 0.10, 0.2, 0.3, 0.5, 1.0, and 3.0 *M*) with the solid barium and strontium carbonates at both 25 and 40°. The finely divided solids, in large excess, were agitated with the various solutions in a shaking device immersed in a thermostat maintained at 25 ± 0.02° and at 40 ± 0.04°. After an interval of twenty-four to forty-eight hours of agitation (some samples were shaken for much longer periods without yielding different results, however), the flasks were allowed to stand for several hours in the thermostat; filtered samples were withdrawn at the thermostat temperature and were immediately titrated against hydrochloric acid, using phenolphthalein as indicator; each sample was heated to the boiling point as the end-point was approached. Weight burets were used throughout. Duplicate equilibrium determinations were made for each concentration and each determination was made in duplicate.

Water.—The best grade of conductivity water was used throughout, the final distillation being made from and into quartz. All water and solutions were protected against carbon dioxide.

The Carbonates.—(a) The barium carbonate was prepared from Merck C. P. precipitated barium carbonate. The carbonate was converted into the bicarbonate to form a very dilute solution; it was then re-precipitated by boiling, collected on a filter, washed with conductivity water, and dried for twelve hours at 250°. (b) The strontium carbonate was prepared from C. P. strontium chloride by the addition, in hot dilute solution, of the required amount of ammonium carbonate of reagent grade. The carbonate was repeatedly washed, filtered and dried for twelve hours at 250°.

The Chlorides.—(a) The lithium chloride was obtained by recrystallizing E. & A. "Pure" lithium chloride. The

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(1) Muir, *J. Chem. Soc.*, **37**, 60 (1880).

(2) Cameron and Robinson, *J. Phys. Chem.*, **11**, 577 (1907).

(3) Cantoni and Goguelia, *Bull. soc. chim.*, [3] **33**, 13 (1905).

(4) Dubrisay and François, *Compt. rend.*, **192**, 741 (1931).

(5) De Coninck and Arzalier, *Bull. acad. roy. Belg.*, 577 (1908).

(6) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, Chapter XXVIII.

(7) (a) Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 241 (1893); (b) McCoy and Smith, THIS JOURNAL, **33**, 468 (1911); (c) Seidell, "Solubilities," D. Van Nostrand Co., New York, 1919, p. 107.

(8) (a) Holleman, *Z. physik. Chem.*, **12**, 135 (1893); (b) Kohlrausch and Rose, *ibid.*, **12**, 241 (1893); (c) ref. 7b, p. 473.