

comparatively small rise in the decomposition temperature is indicated. In all instances, however, the rate of oxygen evolution is significantly increased.

It must be emphasized that the decomposition temperatures recorded refer to true equilibrium conditions, concordant values being obtained with rising and with falling temperature. Disagreement with the results of previous investigators is, in certain systems, very evident. Much of the earlier work in this field is, however, not directly comparable, owing (in large measure) to differences in the physical condition of the materials employed. As far as possible, standard and reproducible methods of preparation have here been adopted.

The results obtained have been tentatively ascribed to the formation of unstable intermediate compounds between the two oxides present. The increased rates of decomposition may be referred to adsorption effects, but the large temperature changes point strongly to the actual participation of the added oxides in the reaction. Direct evidence was given in certain mixtures of the production of relatively stable complexes.

A later article will continue the study of systems of the types here examined, with particular reference to the Brin oxygen process and the important question of "promoters."

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

THE PREPARATION AND STUDY OF THE RARER ALKALI BROMATES. RUBIDIUM BROMATE.

BY HAROLD D. BUELL AND C. R. McCROSKY.

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Some time ago the preparation and some of the properties of cesium bromate were discussed in *THIS JOURNAL*.¹ In the present paper the work has been extended to the rubidium bromate, which like the cesium salt, has had no mention in chemical literature. Some further data on cesium bromate have been added in this paper.

Preparation of Rubidium Bromate.

A sample of rubidium chloride, of doubtful purity, was converted into the alum² and this was recrystallized several times. The solution of the pure alum was digested with an excess of barium carbonate on the hot plate for several hours, and after filtering, treated with barium hydroxide and then with carbon dioxide. After again filtering, the solution gave no tests for traces of aluminum, barium, potassium, cesium or sulfate.

¹ McCrosky and Buell, *THIS JOURNAL*, **42**, 1786 (1920).

² Browning, "Introduction to the Rarer Elements," John Wiley and Sons Co., 1919, p. 15.

It was now treated with an excess of pure bromic acid and allowed to crystallize. The product was recrystallized three times for analysis.

Analysis of the Substance.

The finely powdered salt was dried at 115° until it became constant in weight. The results recorded in the following tables are those obtained from analyses carried out in the same manner as those made in the examination of cesium bromate.¹

TABLE I.
IODIMETRIC METHOD OF ANALYSIS.

Wts. of RbBrO ₃ taken. G.	RbBrO ₃ obtained by analysis. G.	Difference. G.
0.0724	0.0721	-0.0003
0.1129	0.1132	+0.0003
0.1116	0.1111	-0.0005
0.0831	0.0831	0.0000
0.0771	0.0768	-0.0003
0.0591	0.0585	-0.0006
0.0847	0.0839	-0.0008

PRECIPITATION METHOD OF ANALYSIS.

Reduction with Hydrazine Hydroxide.

Wts. of RbBrO ₃ taken. G.	RbBrO ₃ obtained by analysis. G.	Difference. G.
0.1079	0.1083	+0.0004
0.0826	0.0829	+0.0003
0.0897	0.0908	+0.0011
0.1182	0.1183	+0.0001

The Solubilities of Rubidium and Cesium Bromates.

In Tables III and IV appear the values obtained for the solubilities of rubidium and cesium bromates at several temperatures. The method for making the determinations was modeled after that used by Buchanan.³

TABLE III.

SOLUBILITY OF RUBIDIUM BROMATE IN 100 G. OF WATER.

At 25°. G.	30°. G.	35°. G.	40°. G.	
2.994	3.584	4.310	5.104	
2.895	3.578	4.247	5.116	
2.917	3.509	4.295	5.021	
2.917	3.559	4.269	5.092	
2.93	3.55	4.28	5.08	Average

TABLE IV.

SOLUBILITY OF CESIUM BROMATE IN 100 G. OF WATER.

At 25°. G.	30°. G.	35°. G.	
3.627	4.484	5.357	
3.664	4.573	5.410	
3.710	4.525	5.215	
3.66	4.53	5.32	Average

³ Buchanan, *J. Ind. Eng. Chem.*, **12**, 448 (1920).

Melting Points.

The melting points of cesium and rubidium bromates were determined by the use of a platinum-platinum-rhodium thermocouple, inserted in a bath of fused anhydrous zinc chloride.⁴ The salts were placed in capillaries in the bath near the couple. The thermocouple was calibrated by comparing with the accepted melting points of pure potassium dichromate (396°), silver bromide (427°) and thallos chloride (429°). The melting point of cesium bromate was found to be approximately 420°, and that of rubidium bromate 430°. Potassium bromate, even after careful purification, was found to melt at 405°, well below the accepted value of 434°. The same value was obtained when the latter salt was sealed in the capillary. The values, above, are the averages, in each case, of 8 or 10 readings, all of which checked closely.

Crystalline Structure.

The authors are indebted to Dr. Charles H. Richardson, head of the Department of Mineralogy of Syracuse University for the following data on the crystalline structure of the two bromates.

The crystals from the water solution of both bromates were small and cube-like, but the polarizing microscope showed that they were not isometric (or isotropic) but anisotropic. Both bromates gave perfect uni-axial interference figures, showing definitely that they crystallize in either the tetragonal or the hexagonal system. Under the microscope the hexagonal system may yield crystals, cube-like in aspect, but this is not true in the tetragonal system. In a few instances the outlines of the crystals showed, with reasonable certainty, that they belonged to the hexagonal system. Unsuccessful attempts were made to secure crystals large enough to measure the interfacial angles on a reflecting goniometer. From the work done, however, it would seem that both the cesium and rubidium bromates belong to the hexagonal system. Examination showed that they were optically positive.

For determining the index of refraction of the two bromates a definite series of immersion fluids, commonly used as standards, was used. When compared with methylene iodide, with an index of refraction of 1.74; carbon disulfide, 1.768; sulfur dissolved in methylene iodide, 1.83; molten sulfur, 1.93; α -sulfur, 1.95; and β -sulfur, 2.038; it was found that the bromates had a still higher index of refraction. The index of refraction of yellow phosphorus (2.144) was a little below, while the value for mercuric iodide crystals from an aniline-quinoline solution (2.22) was a little above that of the bromates. It appears therefore, that the index of refraction of the bromates falls between 2.144 and 2.22. Further work is necessary for the absolute determination of these indices.

Summary.

Rubidium bromate is prepared by a method similar to the one used in the preparation of cesium bromate.

⁴ THIS JOURNAL, 40, 1662 (1918).

Some comparative solubilities of cesium and rubidium bromates are given.

The approximate melting points and data on the crystalline structure of the bromates are included in this work.

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MANGANESE IN THE CATALYTIC OXIDATION OF AMMONIA.

BY CHARLES SNOWDEN PIGGOT.

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The purpose of the investigation¹ was to study the use of manganese as a constituent of catalysts for the oxidation of ammonia. Inasmuch as a considerable amount of work had been done on the use of manganese dioxide mixed with other metallic oxides as a catalyst for the oxidation of carbon monoxide,² it was decided to investigate these and similar mixtures for the catalytic oxidation of ammonia.

However, it was anticipated that these finely divided active catalysts would, like finely divided platinum, prove to be too active for this purpose and consequently show a low efficiency. It was thought that this could be overcome if these materials were combined as alloys and superficially oxidized.

The investigation is, therefore, divided into two parts: first, the study of the oxide catalysts; and second, the study of manganese alloys.

Oxide Catalysts.

Manganese Dioxide.—Ordinary manganese dioxide was found to have little catalytic effect on the oxidation of ammonia, but when in a state of fine sub-division it acted as a catalyst for this reaction.

It was prepared by adding powdered potassium permanganate to cold conc. sulfuric acid and allowing the permanganic acid thus formed to decompose spontaneously into manganese dioxide and oxygen.³ It was then washed by decantation until free from sulfates, filtered and partially dried on a water-bath. When the water content had been reduced to about 50% it was subjected to a pressure of 2818 kg. per sq. cm. for 24 hours. The resulting cake was broken up and completely dried in a stream of oxygen at 130–140°. When tested⁴ on ammonia this material showed considerable catalytic effect, as is shown in Table I following.

¹ This investigation was carried on throughout part of 1919 and 1920.

² Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213–21 (1920); Rogers, Piggot, Bahlke and Jennings, *THIS JOURNAL*, **43**, 1973 (1921).

³ Fremy, *Compt. rend.*, **82**, 1231 (1876).

⁴ The difficulties associated with the quantitative estimation of oxidized nitrogen as described later in this article applied equally here.